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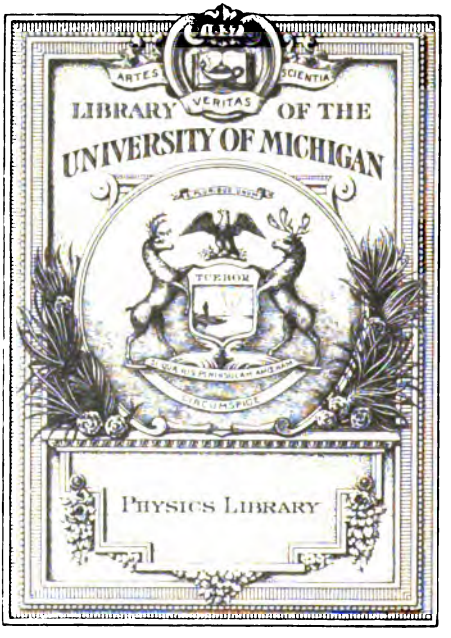
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A TEXT-BOOK OF ELECTRO-CHEMISTRY

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A TEXT-BOOK OF

ELECTRO-CHEMISTRY

BY

MAX LE BLANC

PROFESSOR IN THE UNIVERSITY OF LEIPZIG

TRANSLATED FROM THE FOURTH ENLARGED GERMAN EDITION

BY

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To

HIS TEACHER

PROFESSOR WILHELM OSTWALD

THIS BOOK

IS GRATEFULLY DEDICATED

BY THE AUTHOR

161005

EXTRACT FROM THE AUTHOR'S PREFACE TO THE FIRST EDITION

THE present work was nearly completed in connection with the course of lectures given by me during the winter of 1894–1895. It is meant, first of all, for students of science; for such persons as, having completed their studies, are already in practice; and, finally, for whoever is interested in electro-chemistry. I have endeavored to write as clearly and simply as possible, but those who have but slight previous knowledge must study the book carefully in order to obtain the greatest benefit from it. In modern electro-chemistry there are certain methods of conception which any one studying the subject must make his own, and this cannot be done without work.

M. LE BLANC.

LEIPZIG, September, 1895.

AUTHOR'S PREFACE TO THE FOURTH EDITION

During the three years which have passed since the appearance of the third edition of this book, an abundance of work has appeared in the domain of electro-chemistry. The difficulty of including all of the essentials of the science without unduly increasing the size of the book is continually increasing. I have given my best effort to overcome it.

Up to the present there has appeared an English translation of the first edition, an Italian translation of the second edition, and a French translation of the third edition of this book.

Shortly after the appearance of this, the fourth German edition, an English translation of it will be published.

For assistance in reading the proofs, I am this time indebted to G. Just, Ph.D., and A. König, Dipl. Ing. I am also indebted to Professor Abegg for valuable suggestions.

M. LE BLANC.

Karlsruhe, Baden,
August, 1906.

TRANSLATORS' PREFACE

THE present work is a translation of the fourth German edition, and is essentially a revision and enlargement of that of the first German edition prepared by one of the present translators. Although in its preparation the earlier translation has been freely used, the changes and additions made by Professor Le Blanc, as well as minor additions introduced by the present translators, have either necessitated or rendered advisable the rewriting of a large part of the book. The additions made by the translators have been inclosed in brackets.

Special attention has been given to the following:—

The Notation. A consistent system of notation has been used throughout the book. An outline of it will be found in the Appendix.

The Nomenclature. We have endeavored to make the nomenclature conform to that of the best recent text-books of electricity and chemistry.

The Illustrations. Of the 52 illustrations, 25 are new ones introduced by the translators, and 21 have been redrawn.

Special credit is due Mrs. J. W. Brown for aid in preparing the manuscript and in reading the proofs.

W. R. WHITNEY,
J. W. BROWN.

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A TEXT-BOOK OF ELECTRO-CHEMISTRY

A TEXT-BOOK OF ELECTRO-CHEMISTRY

CHAPTER I

THE FORMS OF ENERGY AND THEIR MEASUREMENT. THE FUNDAMENTAL PRINCIPLES RELATING TO ELECTRICAL ENERGY

Energy and its Forms.—A clear conception of the fundamental principles relating to the forms of energy, especially of electrical energy, is essential to the successful study of electrochemistry. For this reason, before beginning the study of electrochemistry proper, these principles will be considered briefly.

Energy plays a most important part in human affairs. When food or coal is bought, it is the energy content that chiefly concerns the buyer. Similarly when a current of electricity is delivered to the consumer, it is the quantity of electrical energy so delivered that is of greatest importance and that determines the price to be paid.

Energy may be subdivided into five distinct kinds or *forms of energy;* namely:—

MECHANICAL ENERGY,
HEAT ENERGY,
ELECTRICAL ENERGY,
CHEMICAL ENERGY, AND
RADIANT ENERGY.

These forms of energy are mutually transmutable.

The Measurement of Mechanical, Heat, and Electrical Energy.—The units used in the measurement of mechanical energy are grouped into two systems; namely, the Meter-Kilogram-Hour (M. K. H.) System and the Centimeter-Gram-Second (C. G. S.) System. In the former, the technical, system, the unit of mechanical energy or work is that quantity of energy or work which is required to raise a kilogram weight one meter in height. In the centimeter-gram-

second system, which is used in all exact scientific work, the unit of mechanical energy, the erg, is that quantity of energy or work which is required to displace a unit of force through a unit distance. The unit of force, the dyne, is defined to be that force which is required to produce an acceleration of one centimeter per second in a mass of one gram. The relations between these units are represented by the following equations: —

Force (F) in dynes = Mass (M) in grams × Acceleration (A) in centimeters per second.

Mechanical energy (E_m) in ergs = Work (W) in ergs = Force (F) in dynes × Distance (d) in centimeters.

In scientific work, it is very important to distinguish clearly between mass and weight. Mass is an unchangeable property of matter, while weight, since it is the force with which a quantity of matter is drawn toward the earth's center, is a property of matter which varies according to the location on the earth's surface. The unit of mass, called the gram-mass, is defined to be equal to the mass of one cubic centimeter of water at four degrees,[1] the temperature of its maximum density. That mass of any other substance which, under the influence of a given force, receives the same acceleration as does one cubic centimeter of water, under the influence of the same force, may also be taken as a unit of mass. The unit of weight, called the gram-weight, is defined to be that force with which a gram-mass is attracted toward the earth's center. Since this attractive force, at a latitude of 45 degrees and at sea level, produces an acceleration of **980.6** centimeters per second in a gram-mass when falling freely, it is equal to **980.6** dynes.

The relations which exist between the technical unit, the meter-kilogram, and the scientific units, the gram-centimeter, the erg, and the joule, are given by the following equations: —

$$1 \text{ M. Kgm.} = 10^5 \text{ cm. gm.} = 10^5 \times 980.6 \text{ ergs} = 9.806 \text{ joules.}$$

With these units defined, it is now possible to measure and to compare various quantities of mechanical energy, or work.

The unit of heat energy, called the calorie, is that quantity of heat which is required to raise one gram of water from 15° to 16° t.

Having now defined the units for two of the energy forms, it is possible, with the aid of the law of the conservation of energy, to determine the relation between these units. By direct experiment, a

[1] As a matter of fact, however, the unit of mass is one thousandth part of the mass of a certain piece of platinum kept at Paris, which is very nearly one thousand times as great as the above theoretical unit.

known quantity of mechanical energy has been completely transformed into heat energy, showing the following relation between the units of mechanical and those of heat energy: —

$$.1890 \times 10^7 \text{ ergs or } 42720 \text{ cm. gms.} = 1 \text{ calorie.}$$

This relation between the erg or joule and the calorie is called the *mechanical equivalent of heat.*

In an analogous manner, the relations between the units of all the other forms of energy could be found if units for these forms of energy were known. Since, however, besides mechanical and heat energy, only electrical energy has, at present, well-defined units, there remains to be considered an electrical-heat, and an electrical-mechanical, equivalent.

Accepting the transmutability of the energy forms without questioning the conditions under which such transmutation takes place, the case of transference of energy between two systems in contact with each other and containing unequal quantities of the same form of energy will now be studied. This study will be carried out with two gaseous systems possessing different quantities of volume energy, a kind of mechanical energy which may be expressed in terms of the mechanical units already defined.

Let us first consider the system represented by Figure 1, consisting of a gas reservoir G closed by a weightless and frictionless piston p, and placed in the vacuum V. The gas contained in the reservoir is now said to possess a definite volume energy, since it possesses the power of doing a definite quantity of work by expanding against a pressure. If, when the gas supports a 100-gram weight upon the piston, the latter is in the position a, and if, upon heating the gas, the piston and weight are raised to the position b, 50 centimeters above a, a weight of 100 grams is raised 50 centimeters at the expense of the volume energy of the gas. The work done may be expressed as follows: —

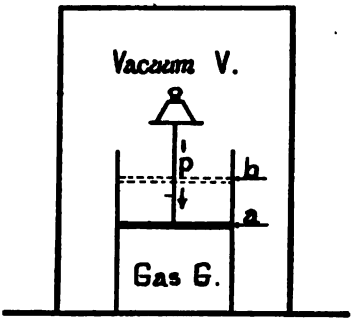


FIG. 1

$$W = F(100 \text{ gms.}) \times d\ (50 \text{ cms.}) = 5000 \text{ gm. cms.}$$

If, now, the piston has a cross section of 100 square centimeters,

each square centimeter of it exerts a pressure of one gram on the gas. The gas is, then, under a pressure of one gram per square centimeter. The volume increase, when the piston rises from a to b, is 5000 cubic centimeters. Hence the product of the pressure, in grams per square centimeter, and the volume, in cubic centimeters, is 5000, a value identical with the number of gram-centimeters of work done during the expansion. The work done may therefore be expressed as follows: —

Work = Pressure (1 gm.) × Volume (5000 cu. cm.) = 5000 gm. cm.

Let us next consider the horizontal vessel represented in Figure 2, which is provided with a movable piston p, on one side of which is hydrogen and on the other nitrogen. If, now, the two gases exert equal pressure upon the piston, it remains motionless and no transference of energy from one gas to the other takes place, although the energy possessed by the nitrogen is much greater than that possessed by the hydrogen. This difference in the energy of the two gases can be made as great as desired by increasing the volume of the nitrogen and decreasing that of the hydrogen, without causing the piston to move. Hence it is evident that the quantity of energy possessed by the two gases does not determine whether or not a transference of energy will take place between them. If, however, we decrease the volume, and thus increase the density and consequently the pressure of one of the gases, the piston is at once set in motion, resulting in an expansion of the gas under the greatest pressure and a corresponding compression of the other. During this change, the gas undergoing expansion loses a definite quantity of volume energy, while that undergoing compression gains the same quantity. When the piston has again come to rest, the same pressure is exerted upon the piston by each of the two gases. *The relative pressures, then, and not the relative volumes of the two gases, determine whether or not a transference of energy will take place between the two gases.*

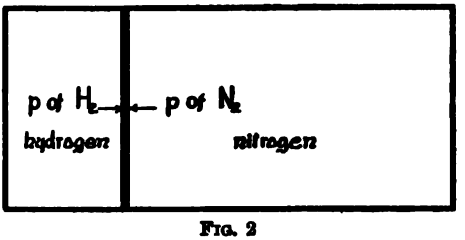


FIG. 2

It has already been shown that the volume energy of a gas may be represented as the product of two factors according to the equation,

$$E_v = pv.$$

The factor p, as shown above, determines the equilibrium of a gaseous system and for this reason is called *the intensity factor.* The other factor v is defined by the equation,

$$v = \frac{E_v}{p} = \frac{\text{Volume Energy}}{\text{Intensity Factor}}.$$

It determines the quantity of volume energy for any given value of the intensity factor p, and is called *the capacity factor.*

A similar resolution of several of the other forms of energy into two such factors has been made, which has greatly facilitated the understanding of energy phenomena. In each case, the following general equations represent the relation between the energy E, its intensity factor f_i and its capacity or quantity factor f_c.

$$E = f_i \times f_c.$$

The intensity and capacity factors of electrical energy E_e are the electromotive force E and the quantity of electricity Q. The relation between electrical energy and its factor is, then, represented by the equation,

$$E_e = \text{E} \times \text{Q}.$$

This will be made clearer in the following pages.

Electric Currents and their Properties. — On account of our limited sense of perception of electrical phenomena, we cannot comprehend them to the extent possible in the case of the phenomena of mechanical energy. In order to comprehend and control them the actions and effects of electrical energy must be studied, for even the idea of a unit of work or of a unit of length, such as the meter, could not be comprehended if the action of a unit of work or the length represented by the meter had not been observed.

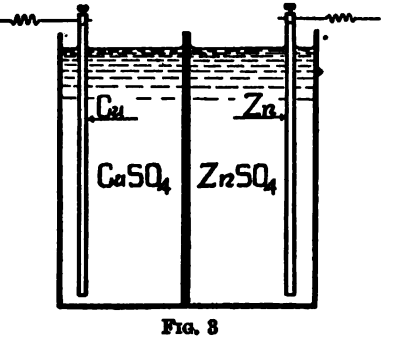


FIG. 3

Consider a vessel divided into two parts by means of a porous plate, e. g., of unglazed porcelain, as shown in Figure 3. If into one part of the vessel is poured a solution of copper sulfate, and into the other a solution of zinc sulfate, and a rod of copper is placed in the copper sulfate solution and a rod of zinc in the zinc

sulfate solution, we have an arrangement called a galvanic cell. If now the zinc and copper rods, the two poles of the cell, be connected by means of a wire, the latter becomes heated. If a magnetic needle be placed near the wire, the needle is turned from its natural position. Finally, if the wire be cut, its two ends fastened to pieces of platinum foil, and these pieces of foil be dipped into a solution of copper sulfate in such a manner that they are not in contact with each other, it is observed that metallic copper deposits upon one of the pieces of platinum.

From these observations, we must conclude that something has taken place in the wire, for the wire always produces these three effects when connecting the zinc and copper poles of the cell and never produces them when disconnected from them. *Whenever a wire produces these effects, a current of electricity is said to be passing or flowing through it.*

It is conceivable that a wire might be found which, when connecting the poles of a galvanic cell, would affect the magnetic needle but not become heated, which, therefore, would not produce all of the three effects stated above to be characteristic of a wire conducting an electric current. This was formerly supposed by many to be true, but, as a matter of fact, such is not the case. From long experience, it is known that whenever a wire produces one of these three effects it always produces the other two, together with a number of other effects which are not of interest at this point. That some of these effects may be made inappreciably small does not contradict the above statement.

These properties of the electric current which serve to detect its presence being known, it is now possible by means of suitable arrangements to study the other properties of the electric current. Considering again the galvanic cell, if the wire is left in its former position with the exception that the end which was joined to the zinc rod is now joined to the copper rod, and the other end is now joined to the zinc rod, the same effects of the electric current are again observed with the simple difference that the magnetic needle is deflected in the opposite direction, and that the metallic copper is deposited upon the other piece of platinum. Therefore we may properly speak of *the direction of an electric current.*

Naturally, the next thing to be determined is whether the deflection of the magnetic needle or the amount of copper deposited upon the platinum in a given time remains constant or varies, and, in the latter case, to determine upon what the variation depends. If, to this end, the connecting wire be lengthened, it is observed that the

rate of the deposition of copper is decreased; while if the wire is shortened, the rate is increased. We must conclude from these facts that the electric current has a strength depending upon circumstances. This gives us the conception of *current-strength of an electric current.*

The current-strength varies inversely as the length of the connecting wire. Therefore the wire hinders or opposes to a certain extent the passage of the electric current, and is said to possess a certain *resistance.*

It has now been observed that the greater the resistance of the wire, the less the current. The question now arises whether or not it is possible to change the current-strength without changing the resistance. Experiment has shown that it is possible to thus change the current. If, instead of using one galvanic cell, two are used, the zinc rod of one cell being connected with the copper rod of the other, as shown in Figure 4, it is observed that a much greater current is obtained, although the resistance of the second cell has been added to that of the wire; that is to say, the electric current starting say at *a* must pass through the wire *ac* and also through the cell II before it reaches the pole *b*. The second cell acts as if it had increased the pressure or force by which the electric current is driven through the wire. Consequently, we come to speak of *the electrical pressure, or electromotive force of the current.*

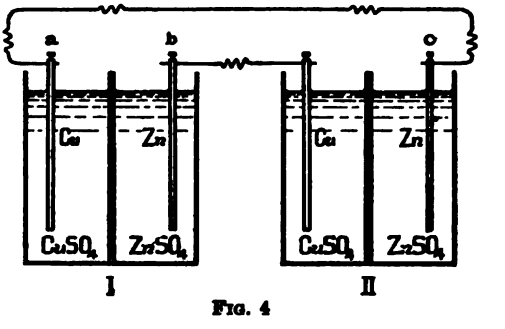


FIG. 4

It is assumed that the terms *current, resistance,* and *electromotive force* are no longer meaningless concepts, but that they possess a real significance to the reader. We may, therefore, proceed to the consideration of the units in which these quantities are expressed. This consideration will be of a much simpler nature than that by which the units were first established.

Electromotive Force, Current, and Resistance. — The electromotive force of a galvanic cell such as has been used in the previous discussion (called the Daniell cell, from its discoverer), when the concentration of the copper sulfate is equal to the concentration of the zinc sulfate, is defined to be **1.10** units, called **volts.** The resistance of a column of mercury, **106.3** centimeters in length and one square milli-

meter in cross section, at 0° t, is defined to be one unit, called an **ohm**. Finally, a current which deposits **0.3294** milligram of copper in a second is defined to be one unit, called an **ampere**.[1] These units may be tabulated, briefly, as follows: —

Unit of E. M. F. = Volt = E. M. F. of the Daniell cell + 1.10.
Unit of current = Ampere = Current which deposits 0.33 mg. of copper per second.
Unit of resistance = Ohm = Resistance of a mercury column, 106.3 cm. × 1 sq. mm.

Why these particular values have been chosen as units need not be discussed here, for this question belongs more to the history of electrical science.

It has already been observed that the current depends upon the electromotive force, on the one hand, and upon the resistance on the other. The assumption was made by Ohm that the current is directly proportional to the electromotive force and inversely proportional to the resistance. This assumption, which is also expressed by the equation,

$$\text{Current (C)} = K\frac{\text{Electromotive force (E)}}{\text{Resistance (R)}},$$

has been found by experiment to be universally true. In this equation, K is a ratio factor, depending on the units in which the current, electromotive force, and resistance are expressed. However, the units defined above are so related that if, in a circuit whose resistance is one ohm, an electromotive force of one volt exists, the current flowing through the circuit is one ampere. Consequently the above factor in this case is equal to unity. Hence the equation,

$$\text{Ampere} = \frac{\text{Volt}}{\text{Ohm}}.$$

With the above units and their mutual relation known, it is now possible to consider how an unknown electromotive force or an unknown resistance may be determined. It is evident that the current in amperes may be determined by simply finding the number of milligrams of copper deposited by the current in one second and dividing by the number of milligrams of copper deposited in the

[1] These terms, *volt*, *ohm*, *ampere*, *coulomb*, *farad* (the last two terms will be explained later), have been derived from the names of the following pioneers of electrical science: Volta, Ohm, Ampère, Coulomb, and Faraday.

same time by a current of one ampere, namely, by 0.3294. This is also expressed by the equation,

$$c \text{ (in amperes)} = \frac{\text{milligrams of copper deposited per second}}{0.3294}.$$

The resistance of the circuit may now be determined by connecting it to the poles of a Daniell cell and measuring the current produced by it in the manner just outlined. If the current is found to be 0.001 ampere, then, since the electromotive force of the Daniell cell is equal to 1.10 volts, the resistance may be calculated by means of Ohm's law as follows:

$$C = \frac{E}{R},$$

$$R = \frac{E}{C}.$$

Then, by substitution of numerical for literal values,

$$R = \frac{1.10 \text{ volts}}{0.001 \text{ ampere}} = 1100 \text{ ohms}.$$

Finally, an unknown electromotive force may be determined by introducing it in the above circuit in place of the Daniell cell, the resistance of the circuit remaining unchanged, and again measuring the current produced in the circuit. If, in this case, the current is found to be equal to 0.01 ampere, then, since the resistance of the circuit is known to be 1100 ohms, the electromotive force may be calculated as follows: —

$$C = \frac{E}{R},$$

or

$$E = CR.$$

Then by substitution of numerical for literal values, —

$$E = 0.01 \text{ ampere} \times 1100 \text{ ohms} = 11 \text{ volts}.$$

In order to obtain a still clearer conception of the electric current, let us consider its analogy to a stream of water. The electromotive force or electrical pressure corresponds to the pressure of the water, the electrical resistance offered by the conductor of electricity to the frictional resistance offered by the conductor of water, and the strength of the electric current to that of the current of water. When a certain current of water is spoken of, it is meant that, in a unit of time, a certain quantity of water passes through a cross

section of the conductor. A unit for water currents has not been established for scientific use, but such a current as would cause one cubic meter of water to pass through a cross section in one second might, for example, be considered to be such a unit.

Just as we speak of the quantity of water in a water current, so we may also speak of the quantity of electricity in the electric current, without necessarily imagining the electricity to be of a material nature. Accordingly, when a current of electricity of one ampere is flowing in a conductor, it is proper to say that a unit quantity of electricity passes through a cross section of the conductor in one second. This unit of quantity of electricity is called the **coulomb**. The total quantity of electricity which passes through a cross section of a conductor is, then, equal to the product of the current by the time during which the current passes. This is expressed by the following equation: —

Quantity of electricity, in coulombs =
Current, in amperes, × Time, in seconds.

In electrical science, it is usual to distinguish between electromotive force and potential or voltage (potential-difference or voltage-difference). The term *electromotive force* is applied to the potential-fall in a cell, which remains a constant value as long as the cell remains constant. It may be compared with the original, constant pressure which forces a quantity of water through a pipe. The term *potential*, or *voltage*, is applied to the variable electrical pressure which is found at different points along a conductor. The distinction between these two terms will be made clearer in the following pages.

In most courses in physics, the following experiment is performed: Water, under a certain pressure, is driven through a narrow, horizontal tube of uniform bore, upon which are a number of upright manometer tubes, as shown in Figure 5.

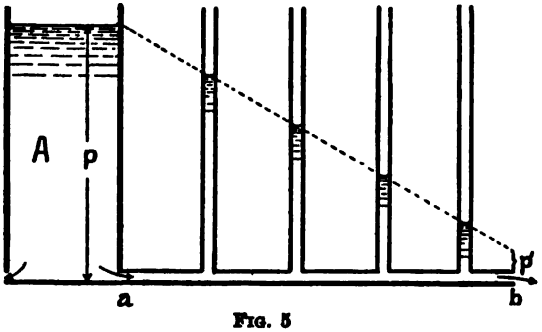


FIG. 5

The height of the water in each of the upright tubes is a measure of the pressure

with which the water is being driven through the horizontal tube at that point. Considering the tube from a to b, it is seen that the pressure of the water decreases in a regular manner from p_w to p'_w, and that with the latter pressure the water leaves the tube. Corresponding to the decrease in pressure along the tube ab, there is a decrease in the quantity of work which can be obtained when a given quantity of water flows through the tube, as will be evident from the following discussion: —

The quantity of work which can be obtained from a given quantity of water Q_w, leaving the reservoir at the point a or c, under a pressure p_w per square centimeter, is equal to $Q_w p_w$. But the quantity of work which can be obtained from the same quantity of water leaving the tube ab at b, under a pressure p'_w per square centimeter, is equal to $Q_w p'_w$. Hence the quantity of water Q_w, in moving through the tube from a to b, has decreased its power to do work from $Q_w p_w$ to $Q_w p'_w$, and the quantity of energy $Q_w p_w - Q_w p'_w$, or $Q_w(p_w - p'_w)$ has, therefore, been consumed in overcoming the resistance which the tube offers to the passage of the water. This quantity of energy has been changed into heat, which has been absorbed by the surroundings and consequently lost. From this it is evident how much depends upon the size of the conducting tube; for the greater the size of the tube the less is the resistance which it offers to the passage of a given quantity of water, and consequently the greater the quantity of available work at its exit.

Similar relations are found in the case of the electric current, as will at once be shown. Consider the wire AB, shown in Figure 6, which represents a complete electric circuit in the form of a straight line. Just as the pressure of the water at different points along the conducting tube was measured by means of upright manometer tubes, so the tension or potential of the electricity along the conducting wire can be measured by an electrometer, an instrument which will be described later on. In this manner the potential at the point A (which is identical with the electromotive force of the circuit) is found to be E, and at the

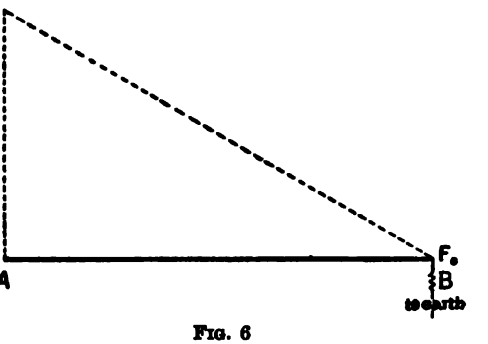


FIG. 6

point B to be zero, when B is connected to the earth by a conductor. Furthermore, just as in the case of the water flowing through the horizontal tube, the quantity of work which can be obtained at the point A from a quantity of electricity Q, at a potential or under an electrical pressure E, is equal to EQ. Similarly, the quantity of work which can be obtained at the point B from the same quantity of electricity at a potential, or under an electrical pressure E_0, is equal to E_0Q, or zero, since E_0 is equal to zero. Hence the quantity of electricity Q, in flowing through the wire from A to B, has decreased its power of doing work from EQ to E_0Q, or to zero, and therefore the entire electrical energy EQ has been changed into heat in overcoming the resistance which the wire offers to the passage of the electricity. The heat has disappeared into the surroundings. The same is true of every electrical circuit in which no work is done.

If now work is caused to be done, as, for example, in the decomposition of a solution, at some point in the circuit almost the entire electrical energy can be transformed into useful work; and, moreover, it is entirely immaterial at what point of the circuit the work is done. Only a small part of the energy, depending upon the material and sectional area of the circuit, is lost as heat to the surroundings. A circuit in which the electric energy is nearly completely transformed into work is represented in Figure 7, where the wire circuit ACB is cut to admit the electrolytic cell at the point C. Along the resulting circuit A to B the electrometer gives the fall in potential as represented in the figure by the dotted line, showing that the fall takes place almost entirely where the work is being done in decomposing the solution. The fall in potential in the same circuit when but one half of the total electrical energy EQ is transformed into work is represented in Figure 8.

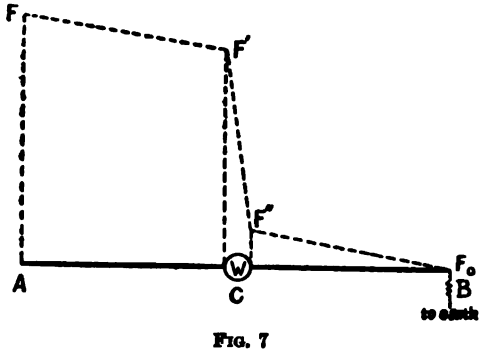


FIG. 7

It is evident, then, that, in an electric circuit, electrical energy may be entirely transformed into heat, or into varying proportions of heat and work, depending upon the nature and arrangement of the circuit.

In an entirely analogous manner, the energy possessed by the water, in the case already considered, may be almost entirely transformed into heat as has been shown, or it may be almost entirely transformed into work, for, if the tube be closed at the point b, the pressure at that point at once rises, as shown in Figure 9, from p'_w to p_w and the maximum quantity of energy, $p_w Q_w$, may then be obtained at b and transformed into work as desired. The current of water differs from the current of electricity in that the former may leave its conductor while still in possession of a certain amount of kinetic energy. This property is not possessed by the latter current.

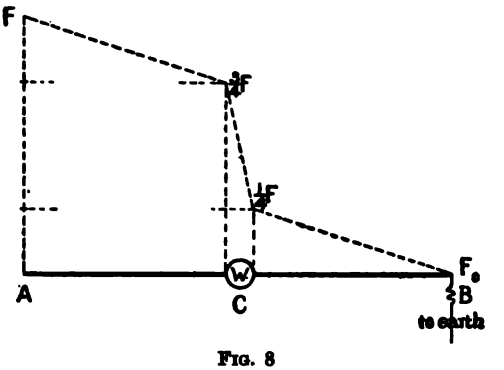


FIG. 8

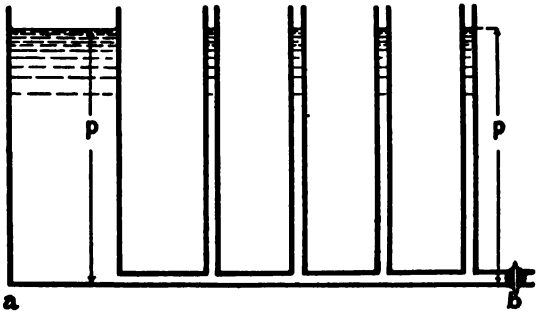


FIG. 9

The fall of potential throughout any galvanic circuit may be presented by the method just employed. If no work is done in the circuit and if the resistance of the circuit is uniform throughout, the potential falls regularly from its highest value at one end to its lowest value, zero, at the other, as represented in Figure 6. If, however, work is done at some point in the circuit requiring a certain quantity of electrical energy and consequently a certain potential, the potential falls by a definite amount at the point where the work is done. Supposing this fall in potential to be equal to F, then the remaining potential $F - F'$ decreases regularly throughout the rest of the circuit

as represented in Figure 7. If, finally, the circuit does not possess the same resistance in every part, *the fall in potential in each part is proportional to its resistance.* Consider, for instance, the circuit represented in Figure 10, where the resistance of *AB* is twice as great as that of *BC* and four times as great as that of *CD*.

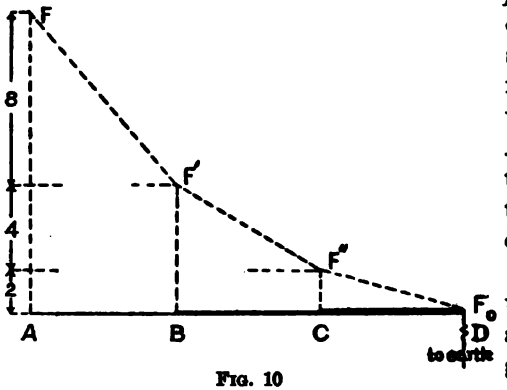


FIG. 10

As shown in the figure, the fall in potential along *AB* is twice as great as that along *BC*, and four times as great as that along *CD*. This relation between the fall in potential in a conductor and its resistance follows of necessity from Ohm's law, which holds for the whole circuit as it does for each part, as will now be shown. In applying the equation which expresses Ohm's law, —

$$C = \frac{E}{R},$$

to any part of a circuit, the value of E is the difference of potential between the two ends of that part, and the value of R is the resistance of the part. Hence in the case represented by Figure 10 the following equations are true, since the current is the same throughout the circuit, whatever the arrangement of the resistances of the parts, as in the case of a current of water flowing through a series of tubes of varying diameters: —

$$C = \frac{E - E_0}{R} = \frac{E - E_1}{R_1} + \frac{E_1 - E_2}{R_2} + \frac{E_2 - E_3}{R_3},$$

where $E - E_0 = (E - E_1) + (E_1 - E_2) + (E_2 - E_3)$ and $R = R_1 + R_2 + R_3$.

It follows from the equations that the potential-difference between the single points must be proportional to the corresponding resistances. Whether the resistance in the circuit is that of a metallic, or of a liquid, conductor, such as a salt solution, or that of a combination of both kinds of conductors, this statement is still true.

If, in a galvanic cell, the poles be connected by a wire, the total resistance of the circuit consists of that of the wire, called the ex-

ternal resistance, and that of the liquid, or liquids, of the cell (for instance in case of the Daniell cell, that of the zinc sulfate and copper sulfate solutions), called the internal resistance. If, now, the external resistance of a Daniell cell is 1000 ohms, and the internal resistance is 100 ohms, while the electromotive force of the cell is 1.10 volts, it follows from the above discussion that the potential-fall in the external part of the circuit, the wire, is 1.00 volt and in the internal part of the circuit, the solution, is 0.10 volt. It is evident that there is a difference between the electromotive force of a cell and the potential-fall in the external part of its circuit, being in the Daniell cell, just considered, 1.10 and 1.00 volts, respectively. If E denotes the electromotive force of the cell, E_1 and R_1, the potential-fall and the resistance in the internal circuit, E_2 and R_2, the potential-fall and the resistance in the external circuit, then the following relation exists between these quantities: —

$$E = E_1 + E_2,$$
$$R = R_1 + R_2,$$

then

$$\frac{E}{E_2} = \frac{E_1 + E_2}{E_2} = \frac{R_1 + R_2}{R_2}.$$

From this relation it follows that the greater the external resistance R_2, the more nearly the fraction $\frac{R_1 + R_2}{R_2}$ approaches the value one, and hence the more nearly the potential-fall in the external circuit E_2 approaches the electromotive force of the cell E. If the external resistance is made infinitely great by breaking the external circuit, these two quantities, E_2 and E, become identical; for on the open circuit there can never be a fall in potential, since this can only take place when current flows, transforming electrical energy into heat or into heat and work. Except when the external resistance is made infinite by breaking the circuit, the potential-fall in the external circuit is always less than the electromotive force of the cell, but approaches the latter as the external resistance approaches infinity or the internal resistance approaches zero.

The Electrical Equivalent of Heat. — From its analogy to the expression for the mechanical energy of water $p_w Q_w$, it has been assumed that the expression EQ represents electrical energy, it being the product of the quantity of electricity by its "pressure" or potential. If the correctness of this assumption be questioned, it is easily possible to prove it to be correct by direct experiment, and, at the same time, to calculate the electrical equivalent of heat. Let us consider, first, a circuit in which there

exists an electromotive force E, expressed in volts, or, in other words, a circuit in which there is a fall of potential from E to 0. It may here be mentioned that the beginner is inclined to fall into error through the former expression by assuming that the value of E remains constant throughout the circuit, which, as seen from the latter expression, is not at all the case. The resistance of the circuit is so chosen that in one second, the quantity of electricity Q, expressed in coulombs, passes through a cross section of the conductor. Since the quantity of electricity passing through a cross section in one second is equal to the current, expressed in amperes, this is equivalent to saying that a current of Q amperes is flowing through the conductor. If now the current performs no work in the circuit, the entire quantity of electrical energy is transformed into heat. Hence the quantity of heat generated in one second when the entire circuit is placed in a calorimeter is equivalent to the quantity of electrical energy which disappears in the same time, or is equivalent to the product EQ, under the assumption that this product correctly represents the electrical energy.

Let us consider, next, a circuit in which an electromotive force $\frac{1}{2}E$ exists, causing a current of two amperes to flow through it. The quantity of heat which would be generated in one second in a calorimeter containing this circuit should be the same as in the former case, since

$$\tfrac{1}{2}E \times 2Q = EQ.$$

Similarly, under the above assumption, whenever the electromotive force and current in any circuit have such values that their product is equal to EQ, the same quantity of heat should be generated in a given time in a calorimeter containing the circuit, for the same quantity of electrical energy would in each case disappear. Experiment has shown that this is actually the case. Moreover, if the resistance of the circuit is such that, with an electromotive force of $2E$ volts, the same current, Q amperes, is produced, then, since the product

$$2E \times Q = 2EQ,$$

twice as much heat should be generated in one second as in the former cases, and so forth. Experiment has proven this also to be true. Therefore the product EQ does represent correctly the quantity of electrical energy.

The calculation of the electrical equivalent of heat is now very simple. The unit of electrical energy is naturally the product of one volt by one coulomb, or one volt-coulomb. It is only necessary

to measure the heat generated when one coulomb of electricity is forced through a circuit by an electromotive force of one volt, or expressed differently, when one coulomb of electricity undergoes a fall in potential of one volt. The resistance of the circuit does not enter into consideration, because the quantity of energy is independent of the time and because the resistance only determines the time required for the fall to take place. If this quantity of heat is x calories, $\frac{1}{x}$ is the electrical equivalent of heat, and represents the number of units of electrical energy which are equivalent to one unit of heat energy.

The electrical equivalent of heat has been found to be:—

1 volt-coulomb = 0.2387 calorie,

or **4.189 volt-coulombs = 1 calorie.**

The mechanical equivalent of electricity is easily calculated from the mechanical and the electrical equivalents of heat.

Since 42720 gram-centimeters = 1 calorie,

then 1 volt-coulomb = 10198 gram-centimeters,

which is *the mechanical equivalent of electricity.*

The quantity of electrical energy which is available when a quantity of electricity Q is forced through a wire by an electromotive force E is equal to EQ. If this energy is completely transformed into heat, then

$$EQ = k \times Q, \tag{1}$$

when Q is the total quantity of heat generated and k is a factor which depends on the ratio existing between the units in which the two forms of energy are expressed. If the corresponding current is represented by C, then

$$EC = k \times q, \tag{2}$$

where q is the quantity of heat generated in a unit of time. But according to Ohm's law

$$C = k' \times \frac{E}{R}, \tag{3}$$

or

$$E = k'RC; \tag{4}$$

then by substitution of this value of E in the equation (2),

we get

$$C^2Rk' = k \cdot q; \quad \text{or if } \frac{k}{k'} = k'',$$

$$C^2R = k'' \cdot q. \tag{5}$$

The last equation may be expressed in words as follows: *The heat energy generated in the whole or in a part of a circuit is proportional to the resistance involved and to the square of the current.* This law was discovered by Joule in 1841 and is known as *Joule's law.* Its experimental verification is a further proof of the validity of Ohm's law. If the quantities C, R, and Q are expressed in amperes, ohms, and calories, respectively, then the number of calories generated in one second is given by the equation, —

$$0.2387 \times \text{amperes}^2 \times \text{ohms} = \text{calories}.$$

The following facts may also be of interest to the readers: —

$$1 \text{ joule} = 10^7 \text{ ergs} = 1 \text{ volt-coulomb}.$$

A certain number of joules, then, denotes a certain quantity of energy independent of the time. If the quantity of energy supplied to a machine in a given time is divided by this time, expressed in seconds, the quotient is the quantity of energy supplied in one second and is called the **power** of the machine. The unit of power,

$$1 \text{ volt-ampere} = 1 \text{ watt} = 1 \text{ joule per second}.$$

The following equations give the relations between the electrical units of power: —

$$\text{Watts} = \frac{\text{Joules}}{\text{Seconds}} = \frac{\text{Volt-coulombs}}{\text{Seconds}} = \text{Volt-amperes}.$$

The power multiplied by the time in seconds gives again the energy supplied during this time. Hence the equations,

$$1 \text{ watt-second} = 1 \text{ joule}$$

and

$$1 \text{ watt-hour} = 3600 \text{ joules}.$$

In technical work the watt-hour or kilo-watt-hour is generally used for the measurement of power instead of joule or kilo-joule, and the ampere-hour instead of the coulomb, for the measurement of quantity of electricity. It may be mentioned that 1 ampere-hour equals 3600 coulombs.

A table showing the relation between the energy units most frequently used may be found at the end of the book.

The Electrical Furnace and its Industrial Importance. — An exact knowledge of the relation between electrical energy and heat which has just been considered is of great importance both in pure science and in technical work. If it is desired to obtain very high tempera-

tures, from, say, 1500° to 3000° and higher, as, for instance, in the manufacture of calcium carbide from calcium oxide and charcoal according to the equation,

$$CaO + 3\,C = CaC_2 + CO,$$

it often happens that electrical heating is the only method of heating by which the required temperature can be reached, or by which commercially favorable conditions can be obtained. The apparatus in which such processes are allowed to take place is called an "electric furnace."

One method of heating, which will be considered in detail, consists in leading two insulated ends of a circuit through two opposite sides of the furnace and connecting them inside the furnace by means of a rod of material of great resistance, such as carbon. The resistance of this rod should be much greater than that of the ends of the circuit leading into the furnace; since the greater the ratio of the internal to the external resistance, the better the utilization of the electrical energy in the furnace. By means of this arrangement it is possible, in a very small space, to convert practically the entire electrical energy supplied to the furnace into heat which is imparted to the reaction mixture packed around the rod. The high temperature attainable is only limited by the inertness and stability of the material of the high resistant conductor. The utilization of the heat is excellent, since the heating is done from the interior. In order to illustrate the thermal effect of the electric current, the following numerical example is given.

Let us consider that an electromotive force of 100 volts is available and that the resistance of the circuit outside of the furnace is 0.001 of an ohm. If now the circuit be completed by means of an inner furnace resistance of 0.999 ohm, then, since the total resistance of the circuit is equal to 0.10 ohm, according to Ohm's law,

$$C = \frac{E}{R},$$

or

$$C = \frac{100 \text{ volts}}{0.10 \text{ ohm}} = 1000 \text{ amperes.}$$

Since the potential-fall in the two parts of the circuit is proportional to the respective resistances, then there will be a potential fall of one volt along the circuit outside, and of 99 volts along the circuit inside of the furnace. Hence 99 per cent of the available electrical energy is transformed into heat in the furnace. The

number of calories of heat generated per second is easily found by either of the following two methods:—

Method A.

1 watt-second = 1 joule = 0.2387 calorie

Watt-seconds = Volts × Amperes = 99 × 1000 = 99,000.

Then the heat generated in

calories per second = 99,000 × 0.2387 = 23,631.

Method B.

$\overline{\text{Amperes}^2}$ × Ohms × Seconds = calories × 0.2387.

or $\overline{1 \text{ ampere}^2}$-ohm-second = 0.2387 calorie.

Number of $\overline{\text{ampere}^2}$-ohm-seconds = $1000^2 \times 0.099 = 99,000$.

Hence number of calories per second = 99,000 × 0.2387 = 23,631.

If the quantity of heat is too great, less electrical energy can be taken from the current source by increasing the resistance inside of the furnace. At the same time, the electrical energy is thus better utilized, since the utilization increases with the value of the ratio of the internal to the external resistance. The quantity of heat required in any given case naturally depends upon the heat of reaction, the heat capacity of the substances, and the loss of heat by conduction and radiation. For commercial work electric furnaces are now built with a capacity of 1000 kilowatts and over, to be operated with a voltage of 50 volts and a current of 20,000, or more, amperes.

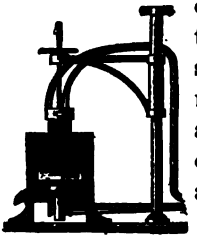


FIG. 11

The internal resistance is very often replaced by an electric arc, especially if it is desired to concentrate the heating on a small surface. The calculation of the heat effect thus obtained is similar to the calculation in the example just considered. It requires only that the potential difference between the two poles and the current be known. Even in the case of the electric arc, it cannot be assumed that the temperature is higher than 3500° *t*, since at that temperature the carbon itself begins to vaporize. The glowing gas of the arc, can, however, be brought to a considerably higher temperature.

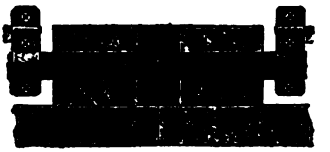


FIG. 12

Models of the electrical resistance furnace of Borchers and of the

electric arc furnace of Héroult are shown in Figures 12 and 11, respectively. These furnaces are on the market in a great variety of forms.

Since in technical work the economy of a process is of first importance, electro-chemical industry has developed mostly in the direction of such processes as may be carried out in the electric furnace. These processes are carried out to advantage when electrical energy may be had at a price of about one quarter of a cent per kilowatt-hour and under. Thus during the last ten or twenty years enormous works have been established in the United States of North America (especially at the Niagara Falls), in France, in Switzerland, and in Norway, which daily transform many millions of meter-kilograms into chemical energy by means of the electric current. In order to give the reader an idea of the magnitude and commercial importance of these works, their products and the importance of them will be briefly considered.

Most of the processes carried out in electric furnaces involve the reduction of oxides by carbon. Borchers was the first to state that in the electric furnace all oxides could be reduced by carbon at a sufficiently high temperature. As a result of this reduction with carbon, pure metal is not necessarily formed, for carbon compounds of the metal may instead be formed.

This is the case in the preparation of calcium carbide, which is made on a very large scale to be used in turn for the preparation of acetylene gas. Calcium carbide is of great interest also from another point of view. Under certain circumstances it is capable of uniting with atmospheric nitrogen to form calcium cyanamide according to the equation,

$$CaC_2 + N_2 = CaCN_2 + C,$$

and the latter compound when treated with steam under pressure is decomposed with the formation of ammonia. This decomposition is represented by the equation,

$$CaCN_2 + 3\,H_2O = CaCO_3 + 2\,NH_3.$$

On the other hand, when calcium cyanamide is leached with hot water and the calcium hydroxide formed is filtered off, the finely crystallizing substance, dicyandiamide, is obtained upon cooling. The reaction is as follows: —

$$2\,CaCN_2 + 4\,H_2O = 2\,Ca(OH)_2 + (CN_2H_2)_2.$$

By fusion with soda, dicyandiamide is transformed into sodium

cyanide and ammonia together with small quantities of tricyantriamide $(CN_2H_2)_3$. Even the latter compound can also be transformed into sodium cyanide and ammonia.

The reactions just described are of great importance because they furnish a means of transforming atmospheric nitrogen into a form which can be utilized. In view of the threatened exhaustion of the great saltpeter deposits, this importance is not to be undervalued.

A further advance in the domain of nitrogen fixation has been made by so conducting the processes that calcium cyanamide is obtained, although not quantitatively, from calcium carbonate, carbon, and atmospheric nitrogen, without the necessity of forming calcium carbide as an intermediate product. The following reaction is involved: —

$$CaO + 2\,C + N_2 = CaCN_2 + CO.$$

The conglomerate, containing the calcium cyanamide, gives on analysis from 12 to 14 per cent of nitrogen. By experiment it has been shown to be a good fertilizer, capable of being used on the soil in its original form.

Besides calcium carbide, silicon carbide (carborundum), valued especially as an abrasive substance, is prepared on a large scale in this way. The following reaction is involved: —

$$SiO_2 + 3\,C = SiC + 2\,CO.$$

Various alloys are prepared in the electric furnace by the reduction of certain minerals. For instance, when chrome-iron ore $(FeO \cdot Cr_2O_3)$ is heated with sufficient carbon an iron-chromium alloy results, containing over sixty percentage of chromium. In a similar manner an iron-titanium alloy, containing a proportion of titanium varying with the conditions of preparation, may be prepared from Ilminite $(FeO \cdot TiO_2)$.

These alloys are used in the production of steel, etc., in order to obtain a definite chromium or titanium content.

Electrical heating is also used to advantage in the production of phosphorus by heating mixtures of the natural phosphates (chiefly calcium phosphate) with carbon and quartz or kaolin. The following reaction takes place: —

$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C = 2\,P + 3\,CaSiO_3 + 5\,CO.$$

The phosphorus which distills off from the mixture is collected under water.

Recently, carbon bisulfide has been prepared from pieces of sulfur and carbon in an electric furnace.

Finally, it may be mentioned that the preparation of the nitrogen oxides by the action of the electric arc upon air has recently received increased attention.[1] The air is forced past an electric arc formed by an alternating current, becoming highly heated and forming a small quantity of the nitrogen oxides. Before these oxides can decompose to any considerable extent, they are rapidly cooled to ordinary temperatures.

In all of these processes, the number of which might easily be increased, the electric current exerts only a heating effect. The electric furnace is, however, also used in processes in which the current is a direct one and exerts both an electro-thermic and an electrolytic action, as, for example, in the process for the preparation of metallic aluminium. In this case, the current furnishes the heat required to maintain the fusion and also decomposes the aluminium compounds dissolved in it with the separation of metallic aluminium at the cathode.

Dark or Silent Electrical Discharge. — The mutual discharge of two oppositely charged bodies, when they are separated by air or any other dielectric, takes place in various ways according as the potential-difference, the distance, and the form of the bodies is varied. It can take place in the form of a dark or so-called silent discharge accompanied by faintly visible streamers of light. Such a discharge differs from the familiar electric arc in that in the former case the passage of electricity takes place only through the gas separating the two electrodes, while in the latter case it takes place chiefly through the vapors formed from the electrodes. If, in the latter case, a constant potential-difference is maintained, the conductance of the electrode vapors increases greatly both the current intensity and the quantity of electrical energy which in the unit of time is transformed into heat.

If the potential-difference between the two electrodes is increased successively, the non-luminous discharge through gases becomes finally an electric arc. Under the usual circumstances, as soon as this transformation takes place, the current suddenly increases to a high value while the potential-difference sinks considerably. It is, in general, not possible to utilize the high potential-difference obtainable by very powerful machines, since the current would increase to such an extent as to cause even the most non-volatile electrodes to volatilize. Nevertheless under certain conditions all

[1] For further particulars see J. Brode, "Oxydation des Stickstoffs in der Hochspannungs flamme. Habilitationsschrift, Karlsruhe" (1905), W. Knapp, publisher, Halle, Saxony.

possible transition phenomena between discharge through gases and through the electric arc can be produced, as, for instance, when the electric current is transmitted chiefly by means of the electrode vapor near the electrode, and undergoing a gradual transition into purely a discharge through gases at greater distances.[1] It would be more correct to characterize the electric arc (which, in the case of the preparation of the nitrogen-oxygen compounds as just described, appears as a quietly burning flame) as a case of discharge through gases. In the case of alternating currents, even with those of high frequency, the discharge is naturally discontinuous. It is in fact possible that every discharge is discontinuous. This is certainly true of spark discharges, which may be considered to be electric arcs of exceedingly short duration. During such discharges the current rises to enormous values. That, in this case, the vapor of the electrodes plays a part in the conduction of the electricity, is shown by spectroscopic observations, and also by the fact that if sparks are allowed to pass between electrodes of the noble metals under water, *colloidal solutions* are formed.

As already indicated, silent discharges (and also spark discharges) may exert a chemical influence on gases. Thus, to a certain extent, hydrogen and nitrogen are made to combine to form ammonia, hydrogen and cyanogen to form hydrocyanic acid, carbon monoxide and water to form formic acid, and oxygen to be transformed into ozone. In one respect this last technically important reaction is very remarkable. While in all the other applications of the alternating current which have been mentioned, only the quantity of heat or the temperature attainable entered into consideration, in this case it appears that the form of the current must be considered. According to the investigations of Warburg,[2] a close relationship exists between the nature of the light at the points of the conductors and the yield of ozone. It is very probable that the formation of ozone should be attributed to photo- or cathodo-chemical action. It is also interesting to note that Warburg found that, for the form of discharge used by him, the direct excels the alternating current.

When the ozone has reached a certain concentration, it ceases to be formed.

Electrical Capacity. — It may be well at this point to explain the term *electrical capacity*, although it has more to do with static elec-

[1] See also O. Lehmann, "Elektrische Lichterscheinungen und Entladungen," W. Knapp, Halle, Saxony (1898).

[2] Drude's *Annalen*, **12**, 988 (1904); **17**, 1 (1905).

tricity than with our present subject. It is to be especially noted that this so-called electrical capacity is quite distinct from the capacity factor of electrical energy, or the quantity of electricity. By electrical capacity is meant the capacity of a body for taking up or holding electricity. This capacity of a body is independent of its material content, but dependent on its size, form, temperature, and surroundings. If two bodies of unequal electrical capacities be charged with the same quantity of electricity, the potential of the two charges will be unequal, and, further, it will be higher on the body of least capacity. If these two bodies be charged with such quantities of electricity that the two charges are at the same potential, the two quantities of electricity will be unequal, and the larger quantity will be on the body of greatest capacity. The electrical capacity is also defined by the following equation: —

$$\text{Electrical capacity } (k_e) = \frac{\text{Quantity of electricity (Q)}}{\text{Potential (E)}}.$$

The unit of capacity is called the **farad**, and is defined to be the electrical capacity of a body upon which a charge of electricity of one coulomb possesses a potential of one volt. The above equation may therefore be written as follows: —

$$k_e \text{ in farads} = \frac{\text{Q, in coulombs}}{\text{E, in volts}}.$$

Positive and Negative Electricity. The Electrometer. — Thus far we have considered the electric current as analogous to the water current. This analogy is especially useful to beginners, as it serves to facilitate the comprehension of electrical phenomena. It is, however, not a perfect one, and care must be taken to prevent misguidances; for an electric current is not as simple as a current of water.

If a solution of copper chloride be introduced into a circuit as previously described, it is observed that, while copper is separating at one of the pieces of platinum, chlorine is separating at the other. If now, from these facts, it is conceived that the copper is transported through the solution to one electrode, then it must also be conceived that the chlorine is transported in the opposite direction to the other electrode. From this movement of ponderable matter in two opposite directions by means of the electric current, it must be assumed that the electric current, unlike the water current, simultaneously possesses two opposite directions. But we know from the science of static electricity that we have to distinguish between two

kinds of electricity, called respectively positive and negative electricity. Hence it may well be concluded that the electric current consists of simultaneous motions of positive electricity with copper particles in one direction and of negative with chlorine particles in the other. This conclusion is supported by the electrometric experiments to be described later.

The conditions in the case of electrical energy differ, then, somewhat from those in the case of mechanical energy, as will now be shown. The product, volume by pressure, has been shown to represent a quantity of mechanical energy. The capacity factor, the volume, is always a positive quantity, since but one kind of volume is known. The product, quantity of electricity by electromotive force, has also been shown to represent a quantity of electrical energy. In this case, the capacity factor, the quantity of electricity Q, may be either positive or negative. For these two kinds of capacity factors, $+Q$ and $-Q$, we have the following laws: *Whenever a quantity* $+Q$ *combines with an equivalent quantity* $-Q$, *a zero quantity always results. Whenever a quantity of positive electricity is produced, there is always produced at the same time an equivalent quantity of negative electricity; and when these two quantities of electricity are brought together again, they completely neutralize each other.*

In the study of electrical phenomena, it is necessary to become accustomed to abstract thinking. It cannot be expected that a quantity of electricity can be made as tangible to us as a quantity of matter. Upon closer consideration it will be seen, moreover, that if the term *matter* is intelligible there is no reason why the term *electricity* or *quantity of electricity* should be unintelligible. Let us first understand clearly what is understood by the term matter. We speak of matter when we recognize a certain number of properties in a given place. One of these properties is the occupying of space or the presence of a certain quantity of volume energy. If, for instance, the quantity of matter be compressed, its volume is diminished and the work done is the equivalent of this compression. Similarly we speak of a quantity of electricity when we recognize a certain number of definite properties in a given place. These properties are not, however, the same as those which characterize the presence of matter. A quantity of electricity does not fill space or possess volume energy, and hence cannot be grasped by the hand.[1] The ques-

[1] It should be noted, however, that Helmholtz and others have attributed an atomic structure to electricity, assuming the existence of positive and negative elementary particles. According to this view we must assume the existence of two new, univalent, and nearly massless elements, namely, positive and negative electrons

tion then often arises: What is the nature of electricity and what is meant by quantity of electricity? The question, What is the nature of matter? however, is but seldom raised. The two questions are equally idle, for the terms matter and electricity are nothing more than expressions or *collective names* for certain groups of definite properties.

Mechanical work may be transformed into electrical energy by rubbing a stick of sealing wax with a woolen cloth. In this case both the sealing wax and the cloth become electrified, the one with positive, and the other with negative electricity. It is a well-known law of nature that whenever electrical energy is produced, it always appears simultaneously in two separate places, although these places may lie exceedingly near to each other.

It is usual to speak of a quantity of electricity, q, as passing through a circuit in the direction in which copper particles are carried during electrolysis, and we too have followed the custom. According to the conceptions of the present, however, when a quantity of positive electricity passes in one direction during electrolysis, a certain quantity of negative electricity passes in the opposite direction. These quantities are carried on the positive and negative ions, respectively. While the quantities of the two kinds of electricity flowing may not be equal, they must always be so related to each other that in all parts of an electrolytic conductor their sum shall be the same. In metallic conduction it is assumed that the electricity which flows is negative (negative electrons). However, since positive electricity flowing in one direction through a metallic circuit produces the same effects as an equal quantity of negative electricity would produce in flowing in the opposite direction, we are justified for the sake of simplicity in speaking of the whole quantity of electricity of an electric current as flowing in the direction of the migration of copper particles. It should, however, be borne in mind that this method of expression is not strictly correct.

Electrical Measurements. — In measurements of any kind it is necessary to establish a zero or starting point. For the intensity factor of heat energy, the temperature, the absolute zero is taken at 273 degrees below the centigrade zero ($-273° t$). For the intensity factor of volume energy, the pressure, the absolute zero is taken as the pressure existing in a vacuum. For the intensity factor of kinetic energy, the velocity, there is no absolute zero point known. Only relative velocities can be measured. For all ordinary measurements the velocity of the earth is considered to be zero, and when, for instance, a body is said to possess a velocity U, it is really

meant that this is the difference between its absolute velocity and the absolute velocity of the earth. Similarly, in the case of the intensity factor of electrical energy, the potential, there is no absolute zero point upon which measurement may be based. As in the case of velocity, an arbitrary zero point has been adopted. Accordingly, zero potential is taken as the potential which exists at the surface of the earth. If it is desired to bring the potential of any point of an electric circuit to the potential zero, it is only necessary to connect this point with the earth by a good conductor, and thus, in a way, make this point a part of the earth's surface.

Electrical potentials are measured by means of electrometers, of which there are many forms, most of which need not be considered here. The principle is the same whatever the form (excepting galvanic electrometers), and may be understood from a description of one of the simplest forms, known as the gold-leaf electrometer, shown in Figure 13.

If the metal rod *c* be connected with the earth, the strips of gold leaf *a* and *b* are brought to zero potential and hang in parallel positions. If now, after disconnecting the electrometer from the earth, it be brought into contact with a point whose potential is to be measured, positive or negative electricity passes from this point to the strips of gold leaf, which immediately separate as shown by the dotted line in the figure. This is due to the electrostatic repulsion of the like kinds of electricity upon them. The greater the potential at the point the greater the quantity of electricity which will pass to the gold leaves and the farther apart they will separate. Consequently, the position of the gold leaves is a measure of the potential of the point. By calibrating the electrometer, and constructing a suitable scale, unknown potentials may be measured directly in volts by means of it.

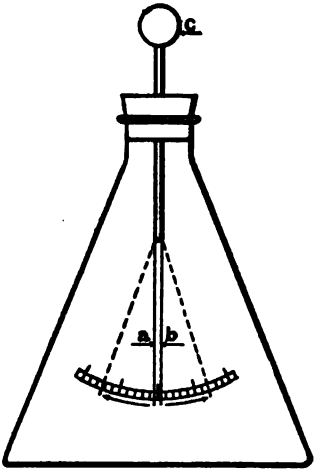


FIG. 13

There remains to be considered a peculiar property of electrical energy, namely, the additivity of the intensity factor, the potential. If we have two sources of such energy, as, for instance, two Daniell cells having the same electromotive force, 1.10 volts, and connect

the source of negative electricity of each, its negative pole, with the source of positive electricity of the other, its positive pole, the resulting combination has an electromotive force equal to the sum of the forces of the two cells, or 2.20 volts. If, on the other hand, like poles are connected, no current flows through the circuit. These two combinations are represented in Figures 14 and 15.

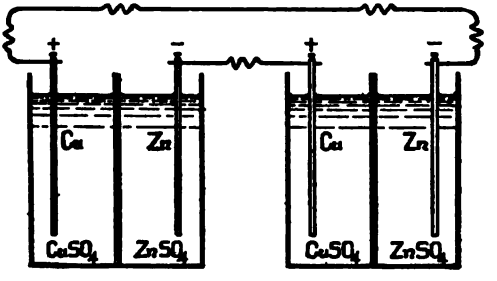


FIG. 14

A very different relation is found, for instance, in the case of the intensity factor of heat energy, the temperature. It is not possible in a similar manner to add two temperatures. If we have two pieces of metal, each having a temperature of 0° at one end and of 100° at the other, they cannot be so combined as to produce a temperature of 200°.

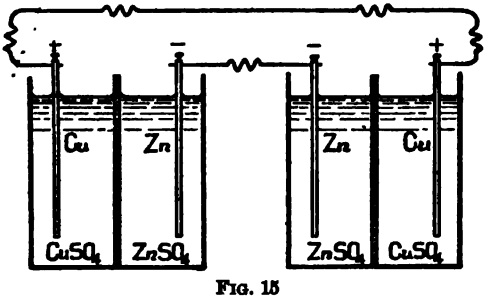


FIG. 15

With electrical energy, when a potential-difference exists between two points, this difference is not altered through a change involving simply an increase in the absolute potential of those points. It is because of this fact that it is possible to produce an electromotive force of any desired magnitude. If the negative pole of a Daniell cell be connected with the earth, at the positive pole there is a potential of + 1.10 volts. If now to this positive pole, the negative pole of a second Daniell cell be connected, then at the positive

pole of the second cell there will be a potential of + 2.20 volts, and so on. Cells thus connected are said to be arranged *in series* or *in tandem*.

Another arrangement, useful for certain purposes, consists in connecting like poles of different cells into groups and then connecting these groups with each other. Although, in this way, no increase in electromotive force over that of a single cell is obtained, the internal resistance of the battery thus formed is less than that of the single cell. These cells are said to be arranged *in parallel*.

Having considered the fundamental principles relating to the electric current, we may now turn our attention to the subject of electro-chemistry itself. As an introduction to this branch of electrical science the history of electricity is briefly presented in the following chapter.

CHAPTER II

DEVELOPMENT OF ELECTRO-CHEMISTRY UP TO THE PRESENT TIME

Earliest Records of Electrical Phenomena. — A little more than two thousand years ago, the first electrical phenomena of which we have record was observed by Thales. He observed that under certain conditions amber (*ἤλεκτρον*) possessed the power of attracting light bodies, such as pieces of paper, feathers, etc. Later, it was found that this property was not confined to amber alone, and then it became known as "*ἤλεκτρον*-like," which later was contracted to the word *electrical*. The phenomena of atmospheric electricity, such as lightning, St. Elmo's fire, aurora borealis, etc., have been known from the earliest times, but their recognition as electrical phenomena is of comparatively recent date.

Up to the beginning of the seventeenth century our knowledge of electricity was extremely scanty and imperfect. At that time, however, it was somewhat increased by the work of William Gilbert. He showed that a great many substances, other than those previously studied, became electrified upon being rubbed, but that none of the metals possess this property. He was the first to declare the necessity of rubbing the material in order to produce electricity.

From this time on an increased interest was taken in electrical phenomena, resulting in the discovery of means for the production of greater electrical effects than were possible through the rubbing of such substances as amber, and in the discovery, by Dufay, in 1733, of the existence of two opposite kinds of electricity. Dufay called the electricity which remains on the glass, vitreous, and that which remains on the resin, resinous electricity.

At the end of the eighteenth century five different sources of electricity were known. The usual, and up to the time of Franklin the only, source of electricity was friction. Franklin discovered that the atmosphere was a second source. A third source was found by Wilke, who observed that electricity was produced when fused substances solidify. This he named "electricitas spontanea." The warming of tourmaline became the fourth source. The fifth and

last source was found in the living animal organism, when the power of certain fish, such as the gymnotus, torpedo, and silurus, to produce electrical shocks was recognized.

The Work of Galvani. — The great electrical discovery of the eighteenth century, the one which attracted the attention of the best investigators of that time, and which has proved to be the discovery of a much more productive source of electricity than was previously known, we owe primarily to the wife of Aloisius Galvani, Professor of Medicine in the University of Bologna. She observed that the freshly prepared hind legs of a frog which were touching a scalpel, moved as if alive while sparks were passing from an electric machine near by. She called Galvani's attention to the phenomenon, and in a short time he was deeply involved in a study of it, considering it a good proof of his pet theory that the animal organism, in general, was in possession of electricity.

In carrying on his experiments he was accustomed to place the preparations of frogs' legs upon an iron railing in the open air. He often watched the contractions taking place in them there, and conceived that it might be due to atmospheric electricity. He observed, further, that when lightning was discharged, or storm clouds approached, contraction in the frogs' legs was most often produced.

Repeating this experiment during a series of calm, clear days, and observing no effect upon the frogs' legs, he twisted the wire which was hooked through the spine of the frog about the iron railing from which the preparation was hanging, thinking thus more easily to discharge any atmospheric electricity which might have accumulated in the preparation. He observed muscular contractions which he then concluded were at least not entirely produced by atmospheric electricity. Later experiments carried on in a room showed him conclusively that these contractions in the frog preparations have nothing to do with atmospheric electricity, and that they can, under certain circumstances, be made to take place in any place at any time.

The breadth of influence of this simple discovery is almost without parallel. It was recognized that the contractions of the frogs' legs were produced by electricity. The question then arose as to the source of this electricity.

Galvani declared that the electricity existed in the preparation, which he compared to a Leyden jar. The muscles, and nerves, according to him, correspond to the two coatings of the Leyden jar, and the wire to the discharging rod. He believed, further, that every animal organism was a source of electricity, to a greater or

less degree, as in the case of the electric eel and certain other fishes, and he hoped through this discovery to be able to penetrate further into the mysteries of life itself.

The Work of Volta. The Voltaic Pile. — For a time, Galvani's opinions were very generally accepted by physicists, many of whom had repeated the above-mentioned experiments. Even Volta, who was a professor in the University of Pavia, and who already had achieved marked distinction, at first was inclined to accept these views. Later, however, he observed that the effects produced were very marked when the back of the frog or the nerve was connected with the leg, or muscle, by a wire the ends of which were of different metals, while the effect was very weak or entirely wanting, when a wire of a single metal was used. *Upon further investigation he found that whenever two metals and a liquid are combined to make a circuit, an electric current is produced.* This showed clearly that the explanation given by Galvani was untenable.

From these experiments Volta concluded that the source of the electricity was either at the point of contact of the two different metals of the circuit, or at the point of contact of the two metals with the liquid. In the case of Galvani's experiments this liquid was the moisture of the preparation. Volta considered the frog's legs, themselves, to be nothing more than *a delicate electroscope, indicating the presence of an electric current in the circuit.* He finally concluded that the principal source of the electricity was at the point of contact of the two metals, and not at the points of contact of metal and liquid. This conclusion has been commonly accepted until within very recent years.

As a sequence of his experiments, it should be mentioned that Volta distinguished, for the first time, between two classes of electrical conductors. In the first class, he included the metals, carbon, and certain other good conducting substances, such as the metallic sulfides; and in the second class, all conducting solutions. This distinction is, in the main, still recognized. According to the prevailing ideas of the present time, conductors of the first class may be defined to be such as conduct the electric current without a movement of ponderable matter, and conductors of the second class, such as conduct the electric current *only* by means of a movement of ponderable matter. The effect of temperature upon the two classes of conductors is remarkable, in that in general, those of the first class conduct electricity less readily, and those of the second class more readily, with increasing temperature. It has also been found to be a fact, which is in agreement with the electro-magnetic theory

of light, that metallic conductors are, even in very thin layers, opaque, while other conductors in thin layers are always more or less transparent to ordinary light. This behavior towards heat and light is a convenient means of distinguishing between the two classes of conductors in such doubtful cases as are met among the oxides.

For conductors of the first class, Volta soon established the contact electromotive series, which is a table of conductors so arranged that if any two of them be connected with each other and also with a conductor of the second class (a liquid thus completing a circuit) an electric current will flow from the conductor higher in the table or series through the liquid to the other. Moreover, the current is greater, the farther apart the two chosen metals stand in the series.

[In the following table is given such a contact-series: —

ZINC
LEAD
TIN
IRON
COPPER
PLATINUM]

After the establishment of the order of contact electromotive forces, Ritter made the discovery, entirely unappreciated at the time, that this order is the same as the order in which metals precipitate one another from solutions of their salts. A reference to the above contact-series will make this clearer. Metallic zinc when placed in a solution of a lead salt dissolves and causes the separation from the solution of metallic lead. Similarly, metallic lead causes the separation of metallic tin, and so on down the series. Moreover, any metal causes the separation of all the other metals of the series which are situated below it, from solutions of their salts. *The identity of the order of the contact electromotive forces of the metals and the order of their precipitating powers shows a relation between electricity and chemistry.* The discovery of this relation may be considered to mark the beginning of scientific electro-chemistry.

A little later, Volta stated his *Law of Contact Electromotive Force.* This law states that the same potential always exists between two given metals, whether they are in contact with each other directly, or only through a series of other metals. [The following table gives the metals in the order of the contact electromotive force series, together with the potential-difference between adjacent metals: —

Metals	Potential-differences in Volts
Zinc	0.210
Lead	0.069
Tin	0.313
Iron	0.146
Copper	0.238
Platinum	0.976

According to the above law, whether zinc be connected with platinum directly or through the series of metals, lead, tin, iron, copper, etc., the difference of potential between them will be 0.976 volt.] It also follows from the above law, that it is impossible to obtain an electric current from a circuit made up entirely of metals; for in such a circuit the sum of all the potential-differences is equal to zero. [This is at once evident from the following diagram: —

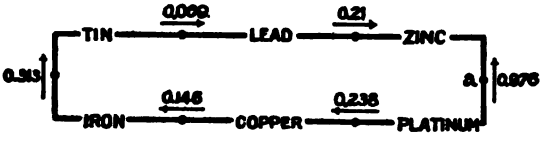


Fig. 16

The sum of the potential-differences at the points of contact of dissimilar metals urging an electric current in one direction (0.21 + .069 + 0.313 + 0.146 + 0.238) is exactly equal to the potential-difference (0.976) urging an electric current in the opposite direction.]

The law of contact electromotive force, according to Volta, does not apply to conductors of the second class. Since he believed that only slight potential-differences were produced at the points of contact of the metals with the conducting liquid, he reasoned that the two metals could be connected with a liquid with scarcely any change in potential from one metal to the other through the liquid. [Accordingly, if the circuit shown in Fig. 16 be broken at *a*, and the two ends dipped in a conducting liquid, a current would flow through the circuit so produced under a potential-difference of nearly 0.976 volt.]

As long as investigators were mainly devoted to the study of frictional electricity, scarcely any attention was given to the relations

between electrical and chemical processes. This was in a large degree due to the fact that the quantities of electricity which were produced by the friction method were too small to bring about any considerable chemical effects. A few facts bearing upon the relation between these two energy forms were known as early as the middle of the eighteenth century. It was known that, by means of electric sparks, metals could be "revived" or obtained from their oxides; that air, other gases, and water were affected by the passage of electric sparks had also been observed. The chemical effect of the electric current was first studied on a large scale after Volta had constructed the apparatus commonly known as the Voltaic pile. [A diagram of this apparatus is shown in Fig. 17.]

It consists of pairs of plates of dissimilar metals, as, for instance, silver and zinc, separated from each other by pieces of absorbent material like blotting paper or flannel cloth, moistened with a liquid conductor such as a salt solution. The strength of the pile depends upon the metals chosen, and upon the number of metallic pairs used in its construction. [Referring to Fig. 17, the greatest potential-difference is obtained between the poles a and b, decreasing as, instead of the pole a, the poles a', a'', etc., are taken.] At the beginning of the present century almost every one who was in a position to do so built a Voltaic pile, and consequently the scientific papers of that period were filled with descriptions of experiments in which the pile was used.

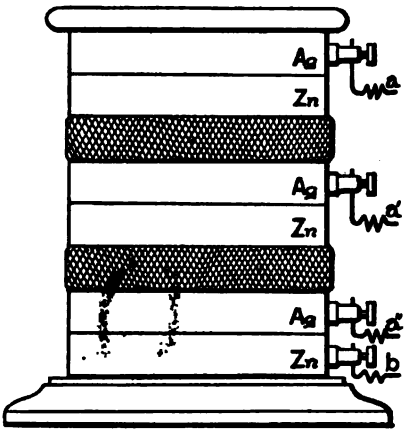


FIG. 17

The Electrolytic Decomposition of Water. — It is worthy of notice that Volta himself says nothing of the chemical actions which may be produced with his apparatus, although it is evident from his experiments that he must have observed the electrical decomposition of water. This indicates that he did not appreciate the significance of this phenomenon. The discovery that water could be decomposed by means of the Voltaic pile thus became the work of others.

In the year 1800 Nicholson and Carlisle showed that on conducting an electric current through water, by dipping the two terminals

of a voltaic pile into it, at one of the terminals hydrogen, and at the other oxygen, was produced. The fact was also not overlooked that the water about the terminal at which hydrogen was produced became alkaline, and that about the other terminal became acid.

Measurement of the Potentials of a Voltaic Pile. — It is surprising that, as early as 1802, thorough measurements of potentials of the Voltaic pile, which are still accepted as correct, were made by Ermann. Some of the results have already been considered in the introduction, and others will now be considered.

Ermann inserted a silver tube, filled with water, into the circuit. The ends of the tube were closed with pieces of glass through which the terminal wires of a battery were passed, making contact with the water inside of the tube. By connecting an electroscope to any desired point of the silver tube, the presence of electricity throughout the tube was shown.

Ermann also established the important fact that *the column of water between the two ends of the battery terminal wires actually contains electricity during the galvanic action.* The fall in potential when the column of liquid forms a part of the circuit still takes place according to the principles discussed on pages 11 to 13. In this case, a sudden fall in potential takes place at the poles due to the work performed there.

When wires are placed between the two ends of the battery wires in the tube as shown in Figure 18, Ermann observed that gas was evolved at each wire end; and that in every case an end at which hydrogen appeared was adjacent to one at which oxygen appeared. This is indicated in Figure 18.

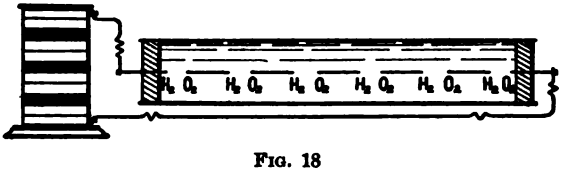


FIG. 18

The electric current was conducted partly by the water and partly by the wires.[1] In this case also, the fall of electroscopic potential took place as in the cases already considered.

[1] If the water has become good-conducting by dissolving oxygen salts, or if the platinum wire is too short, no evolution of gas takes place at the ends of the wire, and the wire takes no part in the conduction of the electric current. The evolution of gas and the conduction of the electric current by the wire takes place appreciably only when the potential-difference between the ends of the

By connecting the circuit with the earth, it is possible to have either positive or negative electricity alone in the column of water and the wires. It is also possible to cause one part of the circuit to exhibit positive, while the rest exhibits negative, electricity.

The Migration of Acid and Alkali, and the Discovery of the Alkali Metals. — It was very difficult for the early investigators to comprehend the formation of hydrogen and alkali at one of the points where the wires from a Voltaic pile came into contact with water, and of oxygen and acid at the other. It was a question with them whether or not the acid and alkali were actually created by the action of electricity on water. Such a question was not absurd, for at that time, the law of the conservation of matter was not at all generally recognized. It was one which required an experimental answer. The task of answering this question was undertaken first by Simon, and then a few years later by Davy, who showed, by a series of very careful experiments, that pure water is decomposed into hydrogen and oxygen by the electric current, without the formation of acid and alkali, and that the formation of the latter, in earlier experiments, was due to the presence of impurities in the water. He performed, furthermore, experiments of the greatest importance upon the migration of acids and bases to the two poles, respectively, for which a satisfactory explanation was not found until the establishment of the accepted theories of the present time. This experiment is briefly described at this point because the phenomena involved should be known. [illegible] be more thoroughly understood after the modern theories have been studied. The reader is advised then to attempt to discover the explanation of this experiment, as thereby he will recognize more fully the advantages of modern conceptions.

If two platinum wires are connected to the poles of a voltaic pile, and the free end of one of them is placed in a vessel filled with pure water, and the free end of the other in one containing a solution of

wire and of the liquid layer parallel to the wire reaches about the value 1.7 volts (the decomposition voltage of water). This process, which is of great industrial importance, cannot be completely understood until the study of polarization (Chapter VIII) is taken up. For a further discussion see Danneel, *Ztschr. Elektrochem.*, **9**, 256 (1903).

When higher current densities are used, the fractional part of the current which flows through the wire becomes greater and greater. This fact has recently received a practical application in the fusion of metals under water by means of large currents of electricity. The water is heated but slightly by the electric current because only a very small part of the current passes through it. Moreover the heating of the water by the glowing metal is reduced to a minimum by the existence of the Leidenfrost's phenomenon.

potassium sulfate, the two vessels being connected by means of a tube filled with water as shown in Figure 19, acid is formed at the wire which is connected with the positive pole of the pile and alkali is formed at the other wire.

The same result is obtained if three vessels, connected in this manner, and filled, respectively, with water, potassium sulfate solution, and water are used with the two platinum electrodes dipping into the end vessels. The positive pole appears to possess an attraction for the acid, and the negative pole for the base, resulting in the decomposition of the salt.

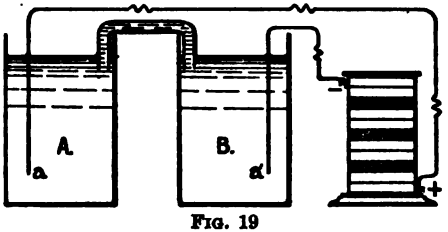


FIG. 19

Davy desired to study the motion of the acid and base towards the positive and negative poles, respectively. He proposed to follow this motion by means of litmus paper, and found to his astonishment, that the first appearance of acid or alkali was not in the water at the point where it came into contact with the salt solution, but at the electrodes, whence it gradually diffused throughout the water. If acid and alkali could thus be made to pass through pure water in going to the poles, without affecting the litmus on the way, Davy questioned whether it was not also possible that they might pass through substances for which they had a great chemical affinity without acting upon them. He found that an interposed concentrated acid solution did not in any way hinder the passage of alkali to its pole, nor did a concentrated alkali solution hinder the passage of acid. There was found, however, in the interposed acid and alkali solutions some of the corresponding salt. This seemed to indicate that the chemical affinity had caused some of the passing compound to be retained. If, further, barium chloride be used to intercept the passage of sulfuric acid, barium sulfate is formed, and only after a long time does sulfuric acid reach its pole. Here, thought Davy, the chemical affinity has completely overcome the electrical attraction.

A little later Davy crowned his experimental work with the discovery of the alkali metals by the separation of them from their fused hydrates by means of the electric current. He thus laid the foundation for the present day commercial preparation of metallic sodium, as, for instance, by the so-called Castner process.

This process consists, principally, in passing an electric current through sodium hydrate which has been heated but slightly above its

point of fusion. The metallic sodium which separates at the cathode is kept from moving away toward the anode by means of a gauze of iron wire of fine mesh. At the anode both oxygen and water are formed. The former is evolved from the fusion to a great extent, while the latter dissolves in the fusion and finally reaches and reacts with the metallic sodium at the cathode, forming there hydrogen and sodium hydroxide. In this way one half of the metallic sodium set free by the current is reconverted into the hydroxide, so that the yield of sodium by this method never exceeds fifty per cent. If the temperature is too high, the metallic sodium also dissolves in the fusion and becomes oxidized at the anode. The yield of metallic sodium finally becomes zero.[1] The following equations represent the process under normal conditions. By the action of the electric current,

$$2\,NaOH = 2\,Na + 2\,OH;$$

at the cathode,

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2;\ \text{and}$$

at the anode,

$$4\,OH = O_2 + 2\,H_2O.$$

The Rise and Fall of the Electro-chemical Theory of Berzelius. — At the time of Davy's great work, Berzelius was just beginning his scientific investigations. In one of the first of these, carried out jointly with Hisinger, he studied the action of the electric current upon solutions of various inorganic substances, resulting chiefly in the establishment of the first electro-chemical theory. This theory dominated the science of chemistry for many decades. According to it, each chemical atom, when in contact with another, possesses, like a magnet, an electro-positive and an electro-negative pole. Moreover, one of these poles is usually much stronger than the other. Consequently an atom behaves as if it possessed but one pole, either electro-positive or electro-negative according as the positive or negative pole, respectively, predominates in strength. The magnitude and sign of this resultant polarity upon the atoms of a given element determines its chemical behavior. If, for instance, the atoms of an element are electro-positive, it will react with elements whose atoms are electro-negative, and conversely. During this reaction, the two kinds of electricities neutralize each other more or less completely, according to the degree of inequality existing between the positive and nega-

[1] For a further discussion see the article by Leblanc and Brode, "The Electrolysis of Fused Sodium and Potassium Hydroxides," *Ztschr. Elektrochem.*, 8, 697 (1902).

tive charges upon the reacting atoms. If complete neutralization does not take place, the resulting compound itself is electro-positive or electro-negative according as the electro-positive are greater or less than the electro-negative charges upon the component atoms. Compounds which thus possess a resultant polarity may then enter into further combinations with each other in such a way as to form a complex compound which is more nearly, or quite, neutral. Thus the theory explains not only the formation of simple compounds from their elements, but also the formation of complex compounds, such as double salts, from their component simple compounds.

The essential elements of the electro-chemical theory may, perhaps, be more easily comprehended from a consideration of a concrete example. Adopting the table of atomic weights used at that time, the oxide of potassium would be represented by the symbol KO. According to the electro-chemical theory, the charge of positive electricity on the potassium atom is greater than that of negative electricity on the oxygen atom, and, consequently, the compound KO still possesses a certain excess charge of positive electricity. Sulfur combines with oxygen, forming the compound SO_3. In this case a negative sulfur atom combines with three negative oxygen atoms, forming the negative compound SO_3. Berzelius explained the energetic action between these two negative substances, by assuming that the sulfur atoms possess a comparatively great positive charge as well as the predominating negative charge, and that the negative charge of the oxygen neutralizes the former. Since the molecules of potassium oxide are positively charged and those of sulfur trioxide negatively charged, these two kinds of molecules may combine chemically with a partial or complete neutralization of their charges, forming $KO \cdot SO_3$. It was supposed that the latter compound still retained a slight positive charge. An entirely similar explanation applies to the formation of aluminium sulfate, $Al_2O_3 \cdot (SO_3)_3$, except that it was supposed that this salt retains a slight negative charge. Assuming the sulfates of potassium and aluminium to be thus oppositely charged, it follows from the theory that it should be possible to cause them to combine with each other. This explains the formation of the double salt, $KO \cdot SO_3 - Al_2O_3 \cdot (SO_3)_3$.

According to the above theory, chemical and electrical processes are closely related, and all compounds have a dualistic nature, being formed of an electro-positive and an electro-negative component. This theory is therefore known as *the electro-chemical or dualistic theory*. It was applied throughout the domain of inorganic chemistry, which at that time was practically the entire science of chemistry,

and although it contained many arbitrary assumptions, it performed a great service to science because of its systematizing influence.

The Laws of Electro-chemical Change. — For several decades after the establishment of the dualistic theory, no considerable advance was made in electro-chemistry. This lack of progress was soon counterbalanced by the important discoveries which were made by Faraday about the year 1835. He was the first to show that, whether electricity is produced by means of friction or by means of a voltaic pile, it is capable of producing the same effects. This fact convinced him that there exists but one kind of positive and one of negative electricity. He next attempted to discover a relation between the quantity of electricity flowing through a circuit and the magnitude of the chemical and magnetic effects which it could produce. His results may be expressed as follows: —

The magnitude of the chemical and of the magnetic effects produced in a circuit by an electric current is proportional to the quantity of electricity which passes through the circuit.

A further discovery was made by Faraday by comparing the quantities of different substances in solution which are decomposed by the same quantity of electricity. This comparison may be made in a very simple manner by connecting into one circuit a series of solutions of different substances so that the same quantity of electricity passes through each solution. The chemical decomposition produced by the electric current in each solution may then be determined by analysis. The results obtained may be summarized as follows: —

The quantities of the different substances which separate at the electrodes throughout the circuit are directly proportional to their equivalent weights, and are independent of the concentration and the temperature of the solutions, the size of the electrodes, and all other circumstances.

The above statement, expressing the relation between the quantity of electricity flowing through a conductor of the second class and the quantity of chemical decomposition which is produced by it, is known as the **law of electro-chemical change**, or **Faraday's law.**

If a solution of an acid, of a mercurous salt, and of a mercuric salt be connected into a circuit by means of platinum electrodes, and the chemical decomposition at the negative electrode be measured in each case, it is found that for every gram of hydrogen liberated in the first solution, two hundred grams of mercury are set free in the second, and one hundred grams in the third. These quantities are identical with the equivalent weights of these elements. The

quantities of mercury separated are to each other as 2 : 1, or inversely proportional to the valences of mercury in the two solutions.

The fact just illustrated, that the quantity of an element deposited by a given quantity of electricity increases the lower its valence in the solution used, is of commercial importance. For instance, the same quantity of electricity deposits twice as much copper from a cuprous chloride (in a sodium chloride solution) as from a cupric chloride solution. Therefore, in obtaining copper by the electrolytic process, the former solution is preferred if other circumstances permit.

The above laws discovered by Faraday, both that relating to the proportionality between the quantity of electricity and the quantity of chemical change which it may produce, and that relating to the deposition of equivalent weights of different substances by the same quantity of electricity, have been proven to hold with great exactness. At the present time, there is no reason for doubting their validity in any case. They hold not only for all solvents, but for fusions as well.

The quantity of electricity which, according to most recent measurements, is necessary to deposit exactly one equivalent weight of any conducting substance is equal to **96,540** coulombs.[1] This number, which will be denoted by ϱ, represents the electro-chemical unit of electricity, and is called the *electro-chemical constant*. The quantity of electricity, ϱ, will then decompose 169.97 grams of silver nitrate with the deposition on the negative pole of 107.93 grams of metallic silver. It follows from these values that the quantity of silver deposited by one coulomb of electricity, or in other words by a one-ampere current in one second, is equal to

$$\frac{107.93}{96,540} = 0.0011180 \text{ gram.}^2$$

It is evident from these figures that in the case of conductors of the second class, *large quantities of electricity move with very small quantities of matter.* In this connection it is interesting to note that, while one hundred coulombs of electricity deposit but 0.111 gram of silver, or but a little more than 0.001 gram of hydrogen, it is sufficient to charge the earth's surface to a potential of more than 100,000 volts.

[1] This value is that adopted by the International Congress for Applied Chemistry held in 1903. It will be used throughout the book. According to the measurements of Richards and Heimrod (*Ztschr. phys. Chem.*, 41, 302, 1902), the value of this constant is 96,580 coulombs.

[2] The table at the end of the book contains the values for many other metals, etc.

The law of electro-chemical change, when first published by Faraday, met with great opposition, due principally to the imperfect conception at that time of the fundamental principles relating to electrical energy and to faulty understanding of the law. Even Faraday himself did not have a clear idea of them. The quantity of electricity, for instance, was not distinguished from the quantity of electrical energy. Now the law refers to quantity of electricity, but not at all to quantity of electrical energy; for it states that when a given *quantity of electricity* passes through any solution, it always produces the decomposition of the same number of chemical equivalents of the solute or solutes. *It states nothing in regard to the quantity of electrical energy necessary to effect this decomposition.* Among those who did not understand correctly the meaning of the law was Berzelius. He understood the law to state that *equal quantities of energy* were required to effect the decomposition of *equal chemical equivalents* of different substances. This made the law seem absurd, for the chemical affinity or cohesion between the particles separated by the electric current in the case of substances differing widely from one another cannot be the same. The factors of an energy are still often mistaken for the energy itself.

Electro-chemical Nomenclature. — Besides discovering the law of electro-chemical change, Faraday also devised the system of electro-chemical nomenclature. To explain the phenomena observed during the passage of electricity through a solution, he assumed that the movement of electricity was associated with a movement of particles of ponderable matter. These particles he called *ions*. Those ions which move in the direction of the positive electricity he called *cations*, and those which move in the opposite direction, *anions*. Substances which conduct electricity with an associated movement of ions, or conductors of the second class, Faraday called *electrolytes*, and to the conduction of electricity by an electrolyte he gave the name *electrolysis*. The name *electrode* he gave to the surface of contact between conductors of the first and second classes of the circuit. That surface to which the cations move received the name *cathode*, and that to which the anions move, the name *anode*. These terms will be used throughout the remainder of the book.

Development of the Present Theory of Electrolysis. The Grotthus Theory. — Those who first recognized the decomposition of water by an electric current, as already indicated, sought an explanation for the simultaneous appearance of hydrogen at one electrode and of oxygen at the other. It was not until 1805, however, that a comprehensive theory for this phenomenon was put forward. During

that year such a theory was published by Grotthus. According to this theory, the electric current charges one electrode positively and the other negatively, and these charged electrodes then exert an electrical influence upon the water molecules. Under this influence the water molecules (then represented by HO) acquire a polarity, the hydrogen atom becoming charged with positive, and the oxygen atom with negative, electricity. The positive electrode then attracts the negatively charged oxygen atom; and the negative electrode, the positively charged hydrogen atom, causing the water molecules to arrange themselves in the order represented by the row *a* in Figure 20. If now the electromotive force applied to the electrodes, and the consequent charge of electricity upon the electrodes, is great enough, the attraction exerted on the atoms 1 and 1′ nearest the electrodes causes the decomposition of their respective water molecules. Each of the attracted atoms then moves to the electrode

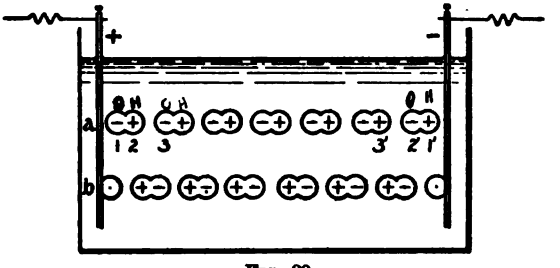


FIG. 20

attracting it, where its charge is neutralized by the charge on the electrode, and it assumes the form of electrically neutral gas. The oxygen and hydrogen atoms 2 and 2′ which are thus left free in the solution, according to the theory, combine with the hydrogen and oxygen atoms 3 and 3′ respectively, of the adjacent water molecules, forming new molecules of water. The action continues with the other water molecules between the electrodes, resulting in a row of new water molecules, arranged as represented in the row *b* in the above figure. Under the attractive forces of the charges on the two electrodes, these new molecules are then orientated like those represented in row *a*, and the process proceeds as before. This explanation satisfied the scientific world for many decades.

The Conductance of Solutions and the Constitution of Ions. — Soon after Grotthus advanced his theory, the question whether the water or the dissolved substance conducted the electric current, and the question as to what constitutes the positive and the negative ions, were exhaustively studied. The opinion was for a long time divided.

In general, it was usual to avoid the former question by simply stating facts without involving any particular conception of the process of electrolysis. For instance, it was a common mode of expression to speak of "water which by the addition of sulfuric acid has become a good conductor," *i.e.* merely a statement of experimental observation. The question regarding the constitution of anions and cations of various dissolved substances also was the subject of considerable disagreement. The opinion advanced by Berzelius was the first to be universally accepted. According to this opinion, in the case of sodium sulfate, $NaO \cdot SO_3$, NaO is the positive ion, or cation, while SO_3 is the negative ion, or anion. These ions move to the cathode and anode respectively, where they combine with water forming alkali and acid. Sometime later the view was expressed that the ions of this salt are Na and SO_4 instead of those given above.

Both of the questions considered in the preceding paragraph were answered by an experiment performed by Daniell. The answer can, however, be considered as decisive only in the light of the conceptions then accepted. Daniell electrolyzed a solution of sodium sulfate and one of sulfuric acid simultaneously in the same circuit, and found that the quantities of hydrogen and oxygen liberated from each solution were the same. He found, further, that the quantities of acid and alkali formed at the electrodes in the salt solution were equivalent to the above quantities of hydrogen and oxygen. The results of the experiments show the conception of Berzelius regarding the ions of sodium sulfate to be untenable. According to his conception, it would require twice as much electricity to form the above quantities of acid and base and also to set free the above quantities of hydrogen and oxygen in the salt solution as it would to set free the same quantities of hydrogen and oxygen in the acid solution. Since both solutions are in the same circuit, it is evident that this is in contradiction to the law of electrochemical change (Faraday's law). In agreement with this law, Daniell explained his experiment by assuming that Na is the positive and SO_4 the negative ion, and that these ions give up their electric charges at the electrodes and then react with water, producing alkali and hydrogen, and acid and oxygen [according to the following equations:—

$$2\,Na + 2\,HO = 2\,NaO + H_2 \text{ (at the cathode)};$$
$$2\,SO_4 + 2\,HO = 2\,HSO_4 + O_2 \text{ (at the anode)}].$$

It follows from this theory that the quantities of acid and alkali

formed in the salt solution must be equivalent both to the quantities of hydrogen and oxygen set free in the same solution and those set free in the acid solution. The requirements of the theory agree then exactly with the results obtained by experiment. It also follows from this theory that the salt alone must have conducted the electricity through the solution; for if the water conducted a part of the electricity, besides the hydrogen set free as a result of the above secondary and purely chemical reaction, there would be a quantity of these two gases set free corresponding to the quantity of electricity conducted by the water. In this case the quantities of acid and alkali formed must always be less than the equivalent of the quantities of oxygen and hydrogen set free. This is contradicted by the experimental results already mentioned.

Later experiments made by Hittorf and Kohlrausch confirmed the explanation of the phenomena of electrolysis given by Daniell. Accordingly, the metals and radicals behaving like metals, such as $H^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $Ag^{\cdot}$, $Hg^{\cdot}$, $Hg^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $NH_4^{\cdot}$, $NH_3(CH_3)^{\cdot}$, etc., are considered to form positive ions, while all remaining atoms or groups, of conducting substances in solution, such as OH', NO_3', Cl', Br', I', $Fe(CN)_6'''$, $Fe(CN)_6''''$,[1] etc., are considered to form negative ions. It is seen here that there are isomeric ions of different valences among both the negative and the positive ions. For instance $Fe(CN)_6'''$ is the negative ion of potassium ferricyanide, and $Fe(CN)_6''''$, its tetravalent isomer, is the corresponding ion of potassium ferrocyanide. It is by means of such ions as those given above, formed almost entirely from the dissolved substance, that electricity is conducted through a solution. *The electrical conductance of a solution is, therefore, a property of the dissolved substance, the solute, and not of the solvent.*

Replacement of the Grotthus Theory by the Clausius Theory.—As science gradually developed, the imperfection of the theory advanced by Grotthus became more and more apparent. According to this theory the splitting of the molecules, which is necessary for the conduction of electricity, cannot take place until the electromotive force is sufficiently great to overcome the affinity or cohesion between the two components of the given compound. As a matter of fact, however, it was found that, under suitable conditions of experiment, it is possible to cause an electric current to pass through a solution even when the electromotive force of the current is extremely small. For example, such an electric current will pass

[1] As recommended by Ostwald, a dot is used to denote a positive charge and a prime to denote a negative charge.

through a solution of silver nitrate between silver electrodes, causing silver to dissolve from one electrode and to deposit upon the other. The entire action thus consists merely in the transfer of silver from one electrode to the other. It follows from what has just been said that Ohm's law holds for all differences of potential, from the smallest upward, in the case of electrolytic conduction.

In order to show still more clearly the incompatibility of the Grotthus theory and experimentally determined facts, let us consider the following illustration: If to each point in a horizontal row of points, a small sphere is held with a certain force X, then a movement of the entire row of spheres in a horizontal direction, such that each sphere moves to the position of the sphere in front of it, can only take place by the application of a force sufficiently great to overcome the force X. Even with the application of such force, a continuous "current" of spheres can only be maintained when the spheres moving away are continually replaced by others. The analogy between this "current" of spheres and the current of molecules assumed by the Grotthus theory is at once apparent.

Clausius was the first to direct attention to the disagreement of the Grotthus theory or conception of electrolysis with facts. Basing his conclusions upon the experimental results already mentioned, he declared "every assumption to be inadmissible which requires the natural condition of a solution of an electrolyte to be one of equilibrium in which every positive ion is firmly combined with its negative ion, and which, at the same time, requires the action of a definite force in order to change this condition of equilibrium into another differing from it only in that some of the positive ions have combined with other negative ions than those with which they were formerly combined. Every such assumption is in contradiction to Ohm's law."

It is a necessary conclusion from the above statement of Clausius that the individual ions must exist uncombined and free to move in the solution. Clausius himself was prevented from drawing this conclusion by the prevailing theories of his time. He chose rather to follow a middle path by assuming that the positive and negative particles of a molecule of a dissolved electrolyte were not firmly combined with each other, but were in a state of vibration, and that often this vibration became vigorous enough to cause the positive part of one molecule to come into the sphere of influence of the negative part of another molecule, with which it then, for a time, vibrates. The positive and negative particles, thus left momentarily free, soon come into the sphere of influence of oppositely charged

parts of other molecules with which they, also, for a time, vibrate. Thus there takes place in a solution a constant exchange between the positive and negative parts of the molecules of the dissolved electrolytes. When now an electric current flows through the solution, an electrical force is exerted in the direction of the current, and the vibration and exchange between the positive and negative parts of the molecules no longer take place with entire irregularity as before, but take place in such a manner that the vibrations become more vigorous and the exchanges more frequent in the direction of the action of the electrical force. If a cross section of the solution be taken perpendicular to the direction of the electrical force, then evidently more positive particles would move through it in the direction of the current of positive electricity or positive direction, than in the direction of the current of negative electricity or negative direction, per unit of time, and similarly more negative particles would move through it in the direction of the current of negative electricity than in the opposite direction. There is, then, a resultant motion of the positive parts of the molecules in the positive and of the negative parts in the negative direction through the cross section. It is by means of this movement of the two oppositely charged parts of the molecules of the dissolved electrolyte that the electric current passes through a solution.

From this discussion it is evident that, whereas Grotthus assumed that the electric current decomposed the dissolved molecules of the electrolyte, Clausius assumed that the electric current merely guides and hastens the charged parts of the molecules toward the oppositely charged electrodes, respectively, during their momentary periods of freedom. The latter theory was generally accepted almost up to the present time.

At about the same time that Clausius advanced his theory, Hittorf began work upon the migration of the ions, and a little later Kohlrausch commenced experiments upon the electrical conductance of solutions. The work of these investigators greatly increased the knowledge of the process of the electrolysis. Making use of their work, Arrhenius in 1887 replaced the theory of vibrating ions of Clausius by the theory of free ions.

Relation between Chemical and Electrical Energy I. — When Volta stated that electricity was produced at the point of contact between two metals (see page 33), the law of the conservation of energy had not been advanced, and therefore he did not know that the energy of the electric current could only be produced at the expense of some other form of energy. He considered perpetual motion to be

possible, and believed also that an arrangement might be devised which would neither wear out nor require attention, and which, moreover, would be capable of furnishing an unlimited quantity of electrical energy. Since the middle of the last century, when the law of the conservation of energy was discovered, these views of Volta of necessity have suffered a change. The chemical reactions which take place between metal and liquid, which earlier were considered insignificant phenomena of the electric current, are now recognized as the source of the electric current. They furnish the energy necessary for its production.

It is remarkable that the source of the electromotive force of the current was assumed to be at the point of contact of the two dissimilar metals. Without the best of reasons, it is clearly inadmissible to consider that the reactions which take place about the electrodes are the source of the electric current and, at the same time, to consider that the source of the electromotive force is situated at another point. It would be quite as reasonable to assume that when a quantity of heat is generated at a given point in a circuit, the rise in temperature corresponding to it takes place at a different point. The simplest assumption is that the source of both electrical energy and electromotive force is at the same point. This assumption is justified as long as it is not shown to be untenable. As a matter of fact, with it, it is possible to explain perfectly the existing relations. At the present time, the electromotive force of a cell is considered to be made up of the sum of the two potential-differences occurring at the surfaces of contact between the two electrodes and the liquid.

After the establishment of the law of the conservation of energy, and after it was recognized that the processes which go on in a galvanic cell give rise to the electrical energy, the question whether or not the chemical energy involved in these processes, as measured by the heat which they generate, is completely transformed into electrical energy, still remained to be answered.

The Daniell cell (see Figure 3) may be represented by the following scheme: —

$$Zn - ZnSO_4 \text{ solution} - CuSO_4 \text{ solution} - Cu.$$

When the cell is in operation, zinc goes into solution and copper separates out. Now the heat generated by the reaction involved is known from thermochemical measurements. When equivalent weights of the substances enter the reaction, it amounts to 25,050

calories. Hence the thermochemical equation, involving two equivalents of the substances in question, is as follows: —

$$CuSO_4 + Zn = ZnSO_4 + Cu + 2 \times 25{,}050 \text{ calories.}$$

If now instead of heat this reaction produces electrical energy, the quantity of the latter produced would be the electrical equivalent of 25,050 calories. The quantity of electrical energy actually produced by the cell can be easily calculated as follows: The quantity of electricity which flows through the circuit when one equivalent of copper is deposited is equal to 96,540, or $\mathfrak{Q}$, coulombs, since it follows from Faraday's law that, whenever one equivalent of any substance is dissolved or deposited electrically, this quantity of electricity always passes through the circuit. The electromotive force of the cell in volts can be measured and the electrical-heat equivalent is known,

$$1 \text{ volt-coulomb} = 0.2387 \text{ calorie.}$$

The electrical energy produced by the cell, expressed in calories, is, therefore,

$$0.2387 \times 96540 \times E \text{ calories.}$$

The chemical energy of the reactions involved is 25,050 calories. If the chemical energy is completely transformed into electrical energy, we have the following equation: —

$$0.2387 \times 96540 \times E = 25050;$$

or

$$E = 1.087 \text{ volts.}$$

Since this value of the electromotive force of the Daniell cell is very nearly identical with the value of the electromotive force found by experiment, it may be concluded that the chemical energy is completely transformed into electrical energy.

Later experiments carried out with other cells gave results not in agreement with this conclusion. The question was finally answered by the theoretical and experimental investigations of Willard Gibbs, F. Braun, and H. von Helmholtz. These investigators showed that there is usually a difference between the chemical energy consumed in a cell and the quantity of electrical energy given out by it. This difference is made evident by an evolution or an absorption of heat by the cell.

CHAPTER III

THE THEORY OF ELECTROLYTIC DISSOCIATION

THE theory advanced by Arrhenius in 1887[1] gave a great impulse to electro-chemical research. By means of it, the relation between well-known facts which formerly seemed to have nothing in common became at once evident. It has also been an invaluable aid in making further discoveries. So fundamentally important has this theory become, that it is considered to be the foundation of the electro-chemical science of to-day. Its development, and then the present status of electro-chemistry in light of the new conception, will therefore be considered in detail.

In 1887 van't Hoff published an article in the first volume of the *Zeitschrift für physikalische Chemie* entitled, "The Rôle of Osmotic pressure in the Analogy between Solutions and Gases." In this article he showed, both theoretically and experimentally, that the gas laws of constant pressure-volume product (Boyle) and of partial pressures (Gay-Lussac) apply also to dilute solutes. He also stated the following very important generalization of Avogadro's principle:

The same number of gaseous or of solute molecules are contained in a given volume of any gas or of any solution, respectively, when, at the same temperature, the gaseous pressure and the osmotic pressure have the same value.

The Laws and Theories relating to Osmotic Pressure. — The meaning of the term *osmotic pressure* may be made clear by a description of an experiment. Consider an apparatus, such as is shown in Figure 21, consisting of a vessel A filled with water and an upright tube B, open above and closed by a semipermeable membrane m below, which contains a quantity of an aqueous solution as, for example, of sugar. The lower end of the upright tube is then submerged in the water contained in A until the water and sugar solution are at the same level a.

The semipermeable membrane is of such a nature as to permit the free passage through it of water but not of sugar molecules. Many skins and precipitates possess such a semipermeable nature. A pre-

[1] *Ztschr. phys. Chem.*, 1, 631 (1887).

cipitated semipermeable membrane may be prepared by closing the lower end of the upright tube with a piece of parchment paper or a piece of unglazed porcelain, and placing in the tube a solution of potassium ferrocyanide and in the vessel *A* a solution of copper sulfate. The two solutions then penetrate the pores of the parchment or unglazed porcelain from opposite sides, and, meeting within, form a precipitate of copper ferrocyanide in the pores. After washing free from the salts used in its preparation, the membrane is ready for use.

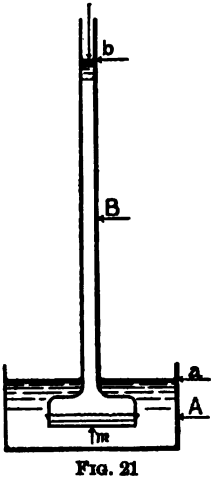


FIG. 21

With the apparatus thus completed and ready for action, it is observed that the surface of the liquid in the upright tube steadily rises, due to the influx of water through the membrane into the sugar solution. In order to prevent the water from entering the upright tube in this way, a definite pressure must be exerted downward on the surface of the sugar solution in *B*. That pressure which is just sufficient to hold the level of the liquid in the tube at its original position *a* is equal to the osmotic pressure of the sugar solution. In the figure, the hydrostatic pressure of the liquid column *ab* is equal to the osmotic pressure. This osmotic pressure exerted by the molecules of solute is analogous to the pressure exerted by gaseous molecules.

The general equation expressing the laws of constant pressure-volume product (Boyle) and of partial pressures (Gay-Lussac) and the principle of equimolecular volume (Avogadro) for all gases is

$$pv = nRT,$$

where p is the pressure exerted by a gas upon a surface of one square centimeter, v its volume, n the number of mols (molecular weights expressed in grams), R a constant, and T the absolute temperature. The expression $\frac{pv}{T}$ has a constant value for one mol of a perfect gas, independent of its nature or concentration. This constant value is represented by R, and is called **the gas constant**. It represents experimentally determined facts, although the theoretical concept, the mol, is involved indirectly. Whenever the molecular volume of any gas in cubic centimeters is multiplied by its corresponding pressure in grams per square centimeters, and the resulting product divided

by the absolute temperature, the value of R is obtained, namely,

$$84800 = 0.8316 \times 10^8 \text{ ergs} = 0.0821 \text{ liter-atm.} = 1.985 \text{ calories.}$$

An equation, identical in form with the above general gas equation, applies to solutes. A consideration of an experiment performed by Pfeffer will make this evident. He found that the osmotic pressure P exerted upon an area of one square centimeter by a one per cent sugar solution at 6.8° t or 279.8° T is equal to 50.5 centimeters of mercury or 50.5×13.59 grams. Since 100 cubic centimeters of the solution contained very nearly one gram of sugar, and since one mol of sugar is 342 grams, the volume of solution V containing one mol of sugar is 34,200 cubic centimeters. Consequently for this sugar solution

$$\frac{PV}{T} = \frac{50.5 \times 13.59 \times 34200}{279.8} = 83900 \text{ (approx.).}$$

This value, within the limits of experimental error, is identical with the value of the constant R, obtained from the analogous expression $\frac{pv}{T}$. It is evident, from this identity of the numerical value of $\frac{PV}{T}$ and $\frac{pv}{T}$, *that the osmotic pressure exerted by the dissolved sugar molecules is equal to the gas pressure which the same molecules would exert if the sugar existed as a gas in the same volume and at the same temperature.*

Having considered the phenomenon of osmotic pressure and the laws which it obeys, it is unnecessary as far as the phenomenon itself is concerned to form special conceptions concerning its mechanism. Since, however, osmotic pressure figures prominently in the discussions in the following pages, and since many new conceptions are most clearly understood by means of their analogy with it, the following hypothetical discussion of the cause of osmotic pressure is given: —

If a sugar solution be placed in a glass tube which is sealed at the bottom, no evidence of osmotic pressure is observable. At the surface of the solution there exists a pressure, called the internal pressure, directed inward at right angles to the surface, amounting to over a thousand atmospheres.[1] In the case of a one per cent sugar solution there is a pressure, the osmotic pressure, amounting to only about one

[1] Experimentally determined facts, which cannot be described here, have necessitated the recognition of such a pressure. Ostwald, *Allgem. Chem.*, Vol. II, page 538, second edition.

atmosphere, directed against this enormous internal pressure. This is due to the dissolved sugar molecules, which act in the water just as they would if they were in the gaseous state and confined in the same volume. Even with very concentrated solutions the internal pressure is still hundreds of atmospheres greater than the osmotic pressure. It is because of this that the vessel containing a solution is not broken by the osmotic pressure which is exerted in the outward direction by the dissolved substance. As it is, only the weight of the solution itself exerts a pressure upon the walls of the containing vessel.

By the employment of a semipermeable membrane, however, evidence of the phenomenon of osmotic pressure may at once be observed. As already noted, when the upright tube in Figure 21 is closed at its lower end with such a membrane, partly filled with a sugar solution, and then set in position as described, water enters through the membrane unless opposed by a pressure in the opposite direction equal to, or greater than, the osmotic pressure of the solution. The solution is bounded by its surface of contact with air and with the walls of the tube and by the porous membrane with which the solution forms no continuous surface, since it is permeable to water. At all the surfaces the internal pressure P_i is exerted inward, and the osmotic pressure of the dissolved sugar P outward, while at the membrane, since there is no liquid surface, only the osmotic pressure P is exerted. Because of this, osmotic pressure is sometimes defined to be the pressure exerted on the membrane by the dissolved substance. Besides the pressure which would be exerted if the tube contained pure water, the solution, then, exerts osmotic pressure which tends to expand it. This expansion can take place, however, only when, by means of a semipermeable membrane, water can enter the solution. It is for this reason that evidence of osmotic pressure is observed only when a semipermeable membrane is used.

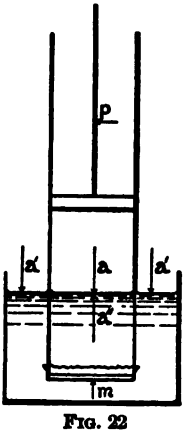


FIG. 22

The rising of the solution in the tube due to pressure exerted by the dissolved substance may perhaps be more easily comprehended by calling to mind the action of a suction pump.

[If water is placed in the tube and outer vessel as shown in Figure 22, it will assume the same level if the downward pressure a and a' are equal. If, however, the downward pressure a is diminished by raising the piston p, water

will flow through the membrane and rise in the tube as in the case of the suction pump. The same movement of water would evidently take place if, instead of decreasing the downward pressure a upon the surface of the water in the tube, an upward pressure a'' against the surface is allowed to act. As already shown, such an upward pressure may be produced by dissolving in the water some substance, as, for example, sugar. Hence it is that the osmotic pressure, which is this upward pressure, causes the liquid to rise in the tube.][1]

The far-reaching analogy which exists between the behavior of gases and of dilute solutes was first pointed out by van't Hoff. He was also able to deduce, from the laws of osmotic pressure, analogous laws applying to phenomena, which, apparently, were not related to osmotic pressure, such as, for instance, the lowering of the vapor pressure or of the freezing point of a solvent by dissolving a substance in it. The laws followed by these phenomena had already been empirically established, principally by Raoult. They may be expressed as follows:—

The lowering of the vapor pressure or of the freezing point of a solvent caused by a dissolved substance is directly proportional to its concentration. The lowering, in each case, for a given solvent is the same for equimolar solutions of all substances. Equimolar solutions contain, in the same quantity of solvent, such quantities of dissolved substances, respectively, as are proportional to their molecular weights. These laws made possible a considerable increase in the knowledge of the constitution of matter, especially in regard to the molecular weights of solutes, or substances in solution. Previously, molecular weights could be determined only in the case of those substances which could be volatilized without undergoing chemical change.

The laws of constant pressure-volume product (Boyle-Mariotte) and of partial pressures (Gay-Lussac) are laws of a limiting condition, holding strictly only for gases at extreme dilution. Therefore, from the analogy which exists between gaseous and osmotic pressures, it would be expected that deviations from the simple laws of solutions would be found in the case of concentrated solutions. Such has indeed been found to be the case when, as has been the custom, the volume involved was taken equal to that of the solution. Recently, however, very surprising results have been obtained by Morse and Frazer[2] in their experimental work on osmotic pressure.

[1] For a more exact definition of osmotic pressure, see Planck, *Ztschr. phys. Chem.*, **42**, 584 (1903).

[2] *Ztschr. Elektrochem.*, 11, 621 (1905).

They found that, even for concentrated solutions (over 30 %), the following statement holds:—

The osmotic pressure exerted by cane sugar in water solution is equal to that which it would exert at the same temperature if it existed as a perfect gas expanded in the volume occupied by the pure solvent.

Calculating in a similar manner, it has also been found that the freezing-point lowering is normal even for concentrated solutions. We may well be impatient to see whether or not this relation, which is without analogy in the gaseous state, obtains generally.

Abnormality of Acids, Bases, and Salts. Electrolytic Dissociation. — One great difficulty presented itself, and cast a dark shadow upon the otherwise bright theory of solutions. Almost all acids, bases, and salts which are soluble in water produce in water solutions a much greater osmotic pressure, vapor-pressure lowering, and freezing-point lowering than that calculated on the assumption that the molecular weights derived from a study of their vapor densities and chemical properties are correct. Corresponding to the abnormality of these properties, the values of the molecular weights of these substances calculated from these properties are, of course, abnormally low.

Not very long before, the molecular theory of gases had been in a similar position, because of the deviations of the vapor densities of a number of substances from the requirements of the theory. It was only with considerable hesitancy that the explanation of these abnormal values on the assumption of a dissociation of the molecules of the gases was then accepted, although at the present time the correctness of this assumption is never doubted. Certainly, it was natural in the light of the close analogy known to exist between the gaseous and the dissolved state, to assume that in solution a similar dissociation takes place. From thermodynamical considerations, the physicist Planck concluded that such a dissociation does take place.[1] This conclusion was not, however, shared by chemists. Indeed, such a supposition seemed absurd, for it required that substances like potassium chloride, in which the atoms were considered to be held together by the strongest chemical affinity, should spontaneously decompose and exist in water solution as potassium and chlorine, in spite of the fact that metallic potassium reacts very energetically with water. Moreover, the supposition seemed to be contradicted by the law of the conservation of energy; for it apparently implied that substances which combine energetically with the generation of much heat may separate again spontaneously.

[1] *Ztschr. phys. Chem.*, 1, 577 (1887).

Before such a radical change could be made in the conceptions of the constitution, in water solution, of these important classes of compounds, it was necessary to remove the apparent contradictions of the new conception to laws of well-proven validity, and also to present strong evidence of its correctness. This was done by Arrhenius.

In an early investigation of the electrical conductance of electrolytes, Arrhenius had already recognized two kinds of solute molecules, namely, active molecules which caused the electrical conductance, and the inactive molecules. He also expressed the opinion that at extreme dilution all the inactive would be transformed into active molecules. He recognized an "activity coefficient" of a solution which is defined by the equation,

$$\frac{\text{Number of active molecules}}{\text{Total number of molecules}} = \text{activity coefficient.}$$

At infinite dilution the value of this coefficient would, then, be unity. For all other dilutions, it would be less than unity and would express the ratio of the equivalent conductance at a given dilution to the limiting value of the equivalent conductance, or the equivalent conductance at infinite dilution. He had not then shown in what respect the active molecules differ from the inactive. As soon as the above-mentioned works of van't Hoff appeared, Arrhenius was able, by comparing the freezing-point lowering produced by electrolytes with the electrical conductance of their solutions, to adduce remarkable and convincing evidence of the correctness of the theory of electrolytic dissociation.

Calculation of the Degree of Dissociation. — As already stated, there is a class of compounds, such as sodium chloride, for example, which give an abnormally large lowering of the freezing point. Thus while one mol of sugar dissolved in ten liters of water lowers the freezing point by about 0.186°, one mol of sodium chloride (considered as NaCl), dissolved in the same volume, lowers it by nearly twice that value. It is evident that, if van't Hoff's principle be accepted as applying to this case, and the sodium chloride be considered as dissociated in solution into a sodium and a chlorine part, the extent of this dissociation may be calculated from a knowledge of the deviation of the freezing-point lowering of the salt from the freezing-point lowering of an undissociated substance.

Let $$\frac{\text{Abnormal freezing-point lowering}}{\text{Normal freezing-point lowering}} = i,$$

where the abnormal value is the value actually determined, and the normal value that which would be obtained if the salt was entirely undissociated.

Then $$i = 1 - x + nx,$$

where x represents the degree of dissociation and n the number of parts into which one molecule dissociates. For the salt NaCl, n is equal to 2, and for $MgCl_2$ 3, and so on.

The degree of dissociation x is then given by the equation,

$$x = \frac{i-1}{n-1}$$

Arrhenius calculated the degree of dissociation, or, as he called it, the affinity constant, for a great many substances from the known values of their freezing-point lowering, and found that the results so obtained agreed with the dissociation values which he obtained from measurements of the electrical conductance. It follows from this, *that only those substances in water solution conduct the electric current which are to some degree dissociated, and that the greater the degree of dissociation the more readily does the substance conduct the electric current.* It is a logical conclusion from these statements that *the conductance of a solution is due entirely to dissociated parts of the molecules.* Arrhenius ascribed electrical charges to these dissociated parts and called them ions.

Even at that time Arrhenius called attention to the fact that many other physical and chemical phenomena were very clearly explained upon the assumption of the existence of free ions in solution.

Dissimilarity between Gaseous and Electrolytic Dissociation. The Ions. — It is evident that there is an important difference between dissociation in the dissolved and that in the vapor state, as, for instance, in the case of ammonium chloride vapor. In the former case only are the parts of molecules resulting from dissociation charged with electricity. The question at once arises as to the source of these charges of electricity which appear suddenly when an electrolyte is dissolved in water. They seem to be produced from nothing. It is not difficult to give a satisfactory answer to this question, as will be evident from the following theoretical discussion. Consider, for example, equivalent quantities of the elementary substances, sodium and iodine. They possess definite quantities of chemical and internal energy. If now they be allowed to react with each other to form sodium iodide, they lose a portion of their chemical or internal energy in the form of heat. The rest of the

energy originally possessed by the sodium and iodine remain associated with the salt, sodium iodide, until some further change is allowed to take place. If the salt be dissolved in water, it dissociates to a large extent, and the chemical or internal energy is again decreased, this time with the appearance of the equivalent quantity of electrical energy in the form of equivalent positive and negative charges on the sodium and iodine ions, respectively. It is evident from this discussion that the sodium and iodine ions differ from the elementary substances, sodium and iodine, in that they possess electrical energy, and also in that their energy content is less. They may be transformed into the corresponding elementary substances again by supplying electrical energy to them by means of an electric current under suitable conditions. When the ions have taken up the requisite quantity of energy, a transformation of electrical into chemical energy takes place, and the sodium and iodine separate at the electrodes as elementary substances.

We may now inquire into the cause of this transformation of chemical into electrical energy when sodium iodide is dissolved in water, and also question the possibility of positively and negatively charged particles existing together in a solution without neutralizing each other. This inquiry and this question is briefly answered by an assumption of the theory of electrolytic dissociation. *This assumption states that the solvent possesses the power of causing this transformation of energy and of preventing the mutual neutralization of the ions.* It may be questioned further whether the assumption of electrically charged particles is of value to science. Experience up to the present time answers this question emphatically in the affirmative.

Ionization according to the Material Conception of Electricity. — According to the material conception of electricity indicated in the note at the bottom of page 26, an ion may be considered to be a compound of positive or negative electrons with the element in question. These two new elements, or electrons, are represented by the symbols, $\oplus$ and $\ominus$. The formation of an ion is, then, entirely analogous to the formation of a compound from two ordinary elements. For instance, in the formation of ions from sodium iodide, the sodium atoms combine with positive and the iodide atoms with negative electrons according to the reaction,

$$NaI + \oplus + \ominus = Na\oplus + I\ominus = Na' + I'.$$

This conception is very comprehensive, for, according to it, the law

of electro-chemical change (Faraday's law, see page 42) appears as a consequence of the laws of definite and multiple proportion.

Although the theory of electrolytic dissociation was not spared great opposition in its early years, it has successfully advanced until at the present time by far the greater number of investigators accept it and recognize its value. As a matter of fact, it possesses the advantages to be expected of a good theory. It correlates a large number of apparently unrelated facts and serves as a good guide for new investigations. At present there is no other theory dealing with the same subject that even approaches this one in usefulness, and for this reason it will be applied throughout the book. *However, it should be borne in mind that it is a theory and not a dogma that is involved, the conclusions from which must be impartially tested by experimentally determined facts.*

CHAPTER IV

THE MIGRATION OF IONS

ACCORDING to the dissociation theory, electrolytes exist in aqueous solution partly in the form of ions, each of which possesses a definite electrical charge. For example, in a solution of hydrochloric acid there are hydrogen ions, $H^{\cdot}$, charged with a definite quantity of positive, and chlorine ions, Cl', charged with an equivalent quantity of negative, electricity. Calling to mind the law of electro-chemical change, or Faraday's law, it may be stated, first, that the conduction of electricity through a solution takes place only by means of a movement of those ponderable particles which are charged with electricity (in the above case, the hydrogen and chlorine ions); and second, that chemically equivalent quantities of these particles are charged with equal quantities of electricity.

A galvanic, or, what is the same thing, an electric, current may be produced in an electrolyte by dipping into it two electrodes which are connected with the positive and negative poles, respectively, of a source of electricity. In consequence of the potential-difference thus produced between the two electrodes, the positive and negative ions move in opposite directions toward their respective electrodes, and an electric current is said to flow through the solution. In all cases the passage of the electric current is accompanied by a decomposition of the electrolyte, even though, in case of a very feeble current, it may not be evident. With hydrochloric acid, electrically neutral hydrogen and chlorine gases separate at the cathode and anode, respectively. An electric current can also be produced in a solution by induction without the use of electrodes. In this case no transformation from the ionic to the electrically neutral state takes place.

When an electric current is conducted through a solution, a certain number of positive ions pass through a cross section of the solution between the electrodes in one direction, and simultaneously a certain number of negative ions pass through it in the opposite direction. It was formerly believed that when the two ions possessed the same valency, the same number of positive and negative ions pass through a cross section in a given time. This belief owed its existence

undoubtedly to the fact that the quantities of the constituents of the electrolyte which separate at the two electrodes are equivalent to each other. It is now known, however, that *seldom or never do equal numbers of the two kinds of ions pass through a cross section of the solution in the same time.* The phenomena of electrical conduction and decomposition are not as closely related as was formerly believed. Their relation was discovered by Hittorf [1] by a careful study of the changes in the concentration of an electrolyte which take place about the electrodes, during the passage of an electric current.

It will now be explained how a knowledge of the relative numbers of the two kinds of ions passing a cross section in a given time, or, what is the same thing, a knowledge of the relative velocities of migration of the two kinds of ions, can be obtained from a study of the concentration changes just mentioned.

As already stated, whenever a current of electricity passes through a solution of an electrolyte, such as of hydrochloric acid, a movement of ions, and a decomposition at the electrodes, takes place. It follows also that, in a solution of such an electrolyte, there are always the same number of negative and positive ions; for if a negative ion separates on the positive electrode as an electrically neutral substance without the simultaneous separation of a positive ion at the negative electrode, the solution afterwards contains more positive than negative ions and hence contains an excess of positive electricity. This excess of positive electricity is large, since the electrical charge upon an ion is very great. If still another negative ion is to be separated alone at the electrode, a greater quantity of work would be required than before, because the positively charged solution would now have a greater attraction for the negative ion and therefore would resist its separation more strongly than before. On the other hand, the separation of a positive ion at the other electrode would require very little work because of the repellent force of the positive electricity of the solution. Since this electrostatic force, compared to the other forces involved, is very great, the decomposition of the electrolyte must take place in such a manner that the positive and negative ions always leave the solution at such rates that the solution itself remains electrically neutral.

The necessity of the separation of equivalent quantities of the two kinds of ions at the electrodes has now been demonstrated. It is known from electrical science that the current, or the quantity of

[1] *Pogg. Ann.*, **89**, **98**, **103**, **106** (1853 and 1859). A reprint of this work may be found in Ostwald's *Klassiker d. exakt. Wiss.*, Nos. 21 and 23.

electricity passing through a cross section of the solution of the electrolyte per unit of time, is the same at all points of the circuit. It is evident also that the total quantity of electricity in motion is equal to the sum of the positive and negative electricities flowing in the circuit, but it does not follow that the ratio of the positive to the negative electricity must remain the same throughout the circuit. Indeed, without contradicting the teachings of electrical science, it may even be assumed that in a given circuit the total quantity of electricity 1, is made up of $\frac{1}{2}$ positive and $\frac{1}{2}$ negative at one point, of $\frac{1}{4}$ positive and $\frac{3}{4}$ negative electricity at another, and so on. Since the motion of one kind of electricity in one direction produces the same effects as the motion of the other kind in the opposite direction, it is justifiable to consider the total quantity of electricity in motion as flowing in one direction, although, in reality, any portion of the total quantity may be flowing in one direction while the rest of it is flowing in the other. It is evident from these statements that there is no necessity for assuming equal velocities for the different ions. This would only be the case when there is a motion of equal quantities of positive and negative electricities at the same rate in opposite directions.

As a matter of fact, seldom or never, when an electric current is flowing through a solution of an electrolyte, do equivalent quantities of positive and negative ions pass through a cross section of the solution in a given time. This is due to the fact that the mobilities of the two kinds of ions are never the same. Thus the mobility of the chlorine ion is far less than that of the hydrogen ion. Corresponding to this difference in mobility, when the two ions are subjected to the action of forces of the same magnitude, as is the case in the electrolysis of a solution of hydrochloric acid, the hydrogen ion moves about five times as fast as the chlorine ion. It must, however, be remembered that the number of positive ions is always equal to the number of negative ions not only in the whole solution, but also, in general, in every part of the solution.

It will be seen later on that it is possible to correlate a large number of facts concerning electrolysis by the assumption that the different ions migrate with different velocities.

The motion or migration of the two kinds of ions may be made more comprehensible by a comparison with the movements of two columns of cavalrymen which are passing each other. Suppose one column proceeding at a walk, the other at a gallop, and imagine a ditch in the way which both columns are crossing at the same time. If the second column moves five times as rapidly as the first, then

five horsemen of the former column cross the ditch in one direction in a certain time, while one of the latter column crosses it in the other in the same time. In all six horsemen pass the ditch. If each horseman carries 100 grams of powder, then, during this time, 600 grams of powder is transported across the ditch, 500 grams, or $\frac{5}{6}$ of it, in one direction and 100 grams, or $\frac{1}{6}$ of it, in the other. In this illustration the two columns of cavalrymen represent the two kinds of particles or ions, and the 100-gram portions of powder, the electrical charge which each particle or ion carries. The case may now be considered in which the cavalrymen and portions of powder are replaced by ions and electric charges.

If a current of electricity be passed through a solution of hydrochloric acid between platinum electrodes, as already stated, the hydrogen ions migrate in one direction with five times the velocity with which the chlorine ions migrate in the opposite direction. Hence when the quantity of electricity 6 passes through the solution, the quantity 5, or $\frac{5}{6}$ of it, is carried by the hydrogen ions, and the quantity 1, or $\frac{1}{6}$ of it, by the chlorine ions. [This will be more evident from a consideration of the following diagrams, in which

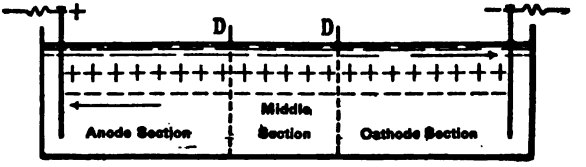


FIG. 23

the hydrogen ions are represented by the symbol +, and the chlorine ions by the symbol −, and the directions in which the ions move when an electric current is passing are indicated by arrows. In Figure 23 a line of twenty-one pairs of hydrogen and chlorine ions are represented between the two electrodes, five of which are situated between the two porous diaphragms D and D, which are permeable to the ions and merely serve to prevent the stirring of the solution by convection currents. This represents the condition of the solution before an electric current has passed. If now a quantity of electricity is passed through the solution sufficient to separate at the two electrodes six ions of chlorine and six of hydrogen, and if the hydrogen ions move five times as fast as the chlorine ions, the condition of the solution at the end of the electrolysis is represented by Figure 24.

Here it is seen that five hydrogen ions have passed from the anode

section into the middle section, and the same number from the middle section into the cathode section, and that in the same way one chlorine ion has passed in the opposite direction from the cathode section and one has appeared in the anode section. Since each ion carries the same quantity of electricity, it is evident that $\frac{5}{6}$ of the total quantity is carried through the middle section by the hydrogen ions, and $\frac{1}{6}$ by the chlorine ions. The number of ions in the middle section has remained constant and need not be further considered. From the anode section six chlorine ions (shown in the vertical column) have given up their charges to the anode and assumed the state of gaseous chlorine, while from the cathode section six hydrogen ions (vertical column) have similarly given up their charges and assumed the state of gaseous hydrogen. The particles of the inert gases are represented by dots on the electrode surface. The anode section has then received by *migration to it* one chlorine ion, and has lost by *migration from it* five hydrogen ions and by *separation at the anode* six chlorine ions. The concentration in the anode section has then decreased from eight pairs of ions to three pairs. From a similar consideration it may be shown that

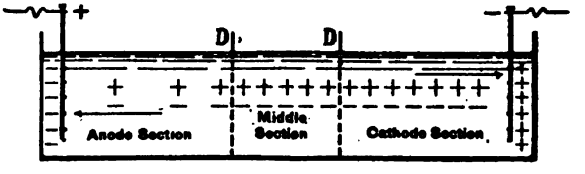


FIG. 24

the concentration in the cathode section has decreased from eight pairs of ions to seven pairs. Therefore the loss in concentration in the anode section is to the loss in the cathode section as five is to one. But this is also the ratio of the velocity of the hydrogen to that of the chlorine ion. Hence the following relation exists between the losses in concentration in the two sections and the corresponding velocities of the two ions: $\frac{10}{2} = \frac{5}{1}$

$$\frac{\text{Loss in the anode section}}{\text{Loss in the cathode section}} = \frac{\text{Velocity of the cation}}{\text{Velocity of the anion}}.$$

Only at the surfaces where the current passes to or from the electrode does the migration of a single kind of ion take place. At these surfaces the conduction of the current consists in the passage of a given quantity of negative electricity directly to the anode, while simultaneously an equivalent quantity of positive electricity passes

directly to the cathode. This explains the fact that *the quantity of the substances which separate at the electrodes, while dependent upon the quantity of electricity which passes, is independent of the velocity of migration of the ions and all other circumstances*, and explains also the fact that changes occur in the concentration of the solutions about the electrodes during electrolysis.

The mechanism of electrolysis being thus illustrated, an actual problem will now be explained. Consider the vessel shown in Figure 25, which is divided into three equal parts by means of porous

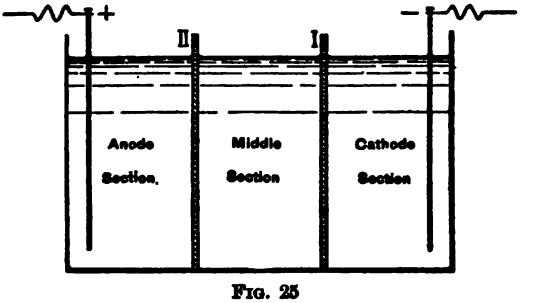


FIG. 25

plates permeable to ions, to be filled with a solution containing 30 equivalents of hydrochloric acid. In each compartment of the vessel there are, then, 10 equivalents of the acid. If now 96,540 coulombs of electricity are passed through the solution, 1 equivalent of hydrogen will separate at the cathode, and 1 of chlorine at the anode. This quantity of these gases may be considered to be removed from the solution. Since the same quantity of electricity passes through every cross section of a circuit, 96,540 coulombs pass through the cross sections of the solution, I and II.

If it is assumed that both ions migrate with the same velocity, then $\frac{1}{2}$ of an equivalent of hydrogen ions, carrying 48,270 coulombs, passes from the anode, through the middle, and to the cathode section, and simultaneously $\frac{1}{2}$ of an equivalent of chlorine ions, also carrying 48,270 coulombs, passes the section in the reverse order. The gain or loss in concentration in the three sections, due to the electrolysis, may now be found. The cathode section has *lost* 1 equivalent of hydrogen ions by separation as a gas at the cathode, and $\frac{1}{2}$ of an equivalent of chlorine ions by migration to the anode, and has *gained* $\frac{1}{2}$ of an equivalent of hydrogen ions by migration from the anode. It has therefore suffered a final loss of $\frac{1}{2}$ an equivalent of hydrochloric acid, and therefore contains, after the electrolysis, $9\frac{1}{2}$ equivalents of the acid. Similarly it may be shown that

the concentration of the solution in the anode section has decreased to $9\frac{1}{2}$ equivalents. The middle section has not suffered a change in concentration, since equal quantities of the two ions have migrated to and from it. [The following summary may serve to make the above concentration changes more comprehensible: —

Original concentration in each section = 10 equiv. HCl,
Quantity of electricity passed = 96,540 coulombs.

	Anode Section		Middle Section		Cathode Section	
	Eq. $H^{\cdot}$	Eq. Cl'	Eq. $H^{\cdot}$	Eq. Cl'	Eq. $H^{\cdot}$	Eq. Cl'
Loss by separation	—	1	—	—	1	—
Loss by migration	$\frac{1}{2}$	—	$\frac{1}{2}$	$\frac{1}{2}$	—	$\frac{1}{2}$
Gain by migration	—	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	—
Total loss	$\frac{1}{2}$	$\frac{1}{2}$	0	0	$\frac{1}{2}$	$\frac{1}{2}$
Final conc. $H^{\cdot}\,Cl'$	$9\frac{1}{2}$		10		$9\frac{1}{2}$	

It follows, then, that when the velocity of migration of the two ions is the same, the solution in both the anode and the cathode section will suffer the same change in concentration.

The hydrogen ions, however, really migrate about five times as fast as the chlorine ions. The above consideration will now be altered as required for this case. Accordingly, $\frac{5}{6}$ of an equivalent of hydrogen passes from the anode, through the middle, to the cathode section, carrying with it $\frac{5}{6}$ of 96,540 coulombs of electricity, while $\frac{1}{6}$ of an equivalent passes through the sections in the opposite direction, carrying $\frac{1}{6}$ of 96,540 coulombs. As before, in total, 1 equivalent of ions passes through the middle section, carrying 96,540 coulombs of electricity. The concentration of the solution in this section remains constant, while that of the solution in the anode and cathode sections changes. The solution in the cathode section has lost by separation at the cathode in gaseous state 1 equivalent of hydrogen ions, and by migration to the anode section, $\frac{1}{6}$ of an equivalent of chlorine ions, and has gained $\frac{5}{6}$ of an equivalent of hydrogen ions by migration from the anode section. Consequently the concentration in the cathode section has been decreased by $\frac{1}{6}$ of an equivalent of hydrochloric acid, and is, therefore, after the electrolysis, equal to $9\frac{5}{6}$ equivalents. The solution in the anode section has lost, by separation at the anode, 1 equivalent of chlorine ions, and by migration to the cathode section,

$\frac{4}{5}$ of an equivalent of hydrogen ions, and has gained, by migration from the cathode, $\frac{1}{5}$ of an equivalent of chlorine ions. It has then suffered a loss of $\frac{4}{5}$ of an equivalent both of hydrogen and of chlorine ions, and hence its concentration has fallen to $9\frac{1}{5}$ equivalents of hydrochloric acid.

[The foregoing may be restated briefly as follows:—

Original concentration in each section = 10 equivalents $H^{\cdot}$ Cl'.
Concentration in middle section remains constant.

	Anode Section		Cathode Section	
	Eq. $H^{\cdot}$	Eq. Cl'	Eq. $H^{\cdot}$	Eq. Cl'
Loss by separation	—	1	1	—
Loss by migration	$\frac{4}{5}$	—	—	$\frac{1}{5}$
Gain by migration	—	$\frac{1}{5}$	$\frac{4}{5}$	—
Total loss	$\frac{4}{5}$	$\frac{4}{5}$	$\frac{1}{5}$	$\frac{1}{5}$
Final concentration $H^{\cdot}$ Cl'	$9\frac{1}{5}$		$9\frac{4}{5}$	

To summarize, after 96,540 coulombs of electricity have passed through the solution, it is found that that part of it contained in the cathode section has suffered a change in concentration from 10 to $9\frac{4}{5}$ equivalents, or a loss of $\frac{1}{5}$ of an equivalent of hydrochloric acid, and that part contained in the anode section a change from 10 to $9\frac{1}{5}$ equivalents, or a loss of $\frac{4}{5}$ of an equivalent of hydrochloric acid. Here, as was found in the diagrammatic illustration of the electrolysis of hydrochloric acid, the loss in the cathode section is to the loss in the anode section as the velocity of the anion is to the velocity of the cation.] In this case of hydrochloric acid this ratio is 1:5. This may also be expressed as follows:—

$$\frac{\text{Loss in the cathode section}}{\text{Loss in the anode section}} = \frac{\text{Velocity of anion } (Cl')}{\text{Velocity of cation } (H^{\cdot})} = \frac{1}{5} \text{ (for HCl).}$$

It was in the manner just indicated that Hittorf was able to determine the relative velocities of migration of the different ions from the changes taking place in the concentration of the solution near the electrodes. His conclusions, although at first opposed, are now generally accepted.

From a superficial consideration of the theory of the independent migrations of the ions, it seems evident that if one ion migrates with a greater velocity than the other, an accumulation of anions

around one electrode and of cations around the other must result during electrolysis. That this is not the case has, however, already been demonstrated. A further question which naturally presents itself is: How can 1 equivalent of chlorine separate at the anode, when only $\frac{1}{6}$ of an equivalent is brought into the anode section by migration? This is answered by assuming that there is always a large excess of ions in the immediate vicinity of the electrode, so that in any given time more ions may separate on the electrode than reach it by migration. This action is assisted by ordinary liquid diffusion.

The ratio of the migration velocities of any two ions may be determined in a very simple manner by the method indicated in the above illustrative problem. It is only necessary to divide the solution of known concentration into three parts, as shown in Figure 25, and, after the passage of a known quantity of electricity through it, to determine the concentration changes which have taken place in each part. The concentration of the middle portion must remain constant. If this is not the case, it shows that the portions of solution about the electrodes have diffused into this section, thus destroying the value of the determination. Such a change in the concentration of the middle portion often takes place when the electrolysis is too long continued.

In general, the quantity of the substance migrated or transferred, and not the quantities "lost" about the electrodes, is used in calculations. If one equivalent of the anion and one of the cation is separated at the electrodes, and if the fraction of an equivalent n_a of the anion is transferred from the cathode to the anode section, then the fraction $1 - n_a$ of the cation must have migrated from the anode to the cathode section. These experimentally determinable quantities, n_a and $1 - n_a$ (or n_c), are called the *transference numbers* of the anion and cation, respectively, and their ratio is equal to the ratio of the velocities of migration of the ions. This is expressed by the equation

$$\frac{n_a}{1 - n_a} = \frac{\text{Velocity of the anion } (u_a)}{\text{Velocity of the cation } (u_c)} = \frac{\text{Loss at the anode } (L_a)}{\text{Loss at the cathode } (L_c)}.$$

From this equation it follows that

$$n_a = \frac{u_a}{u_c + u_a}, \text{ and } 1 - n_a = \frac{u_c}{u_c + u_a}.$$

Thus it is evident that n_a and $1 - n_a$ are equal to the ratios of the migration velocity of the anion and cation, respectively, to the sum

of the two migration velocities. Because of this relation n_a is also called the *relative migration velocity* of the anion, and $1 - n_a$ that of the cation.

Up to the present, only univalent ions have been taken into consideration. However, the transference numbers of di- or polyvalent ions may be determined in an analogous manner. If we consider, for instance, a divalent ion which is associated with two oppositely charged univalent ions, as in the case of $Ba^{\cdot\cdot}\begin{matrix}Cl'\\Cl'\end{matrix}$, then $\frac{n_a}{1-n_a}$ represents the ratio of the migration velocity of both chlorine ions to that of the barium ion.

Although the relative migration velocities, and therefore also the ratio of the migration velocities, can thus be determined, the absolute value of each velocity cannot be found by this method. (See the chapter on the conductance of electrolytes.)

For the sake of clearness it should be remarked at this point that, by the term *mobility* or *migration velocity* is meant the velocity with which one equivalent of an ion moves when acted upon by a unit force. Since, when acted upon by any other force, the velocity varies with that force, the ratio of the velocities of the ions produced by any given force is equal to the ratio of the migration velocities. This subject will be further considered in the section on the absolute migration velocities of ions.

In carrying out a determination of the relative migration velocities of the ions, naturally the quantity of the ions separated at the electrodes as electrically neutral substances must be taken into account. An example taken from Hittorf's work will now be considered, in order to show how the calculation of results is most easily made.

A four per cent solution of silver nitrate was electrolyzed at 18.4° for a considerable time, and the quantity of silver deposited and the change in concentration about the cathode determined: —

Quantity of silver deposited and thus removed from the solution about the cathode . . . . = 0.3208 gram.
Quantity of silver contained in a volume V of the solution about the cathode before electrolysis = 1.4751 grams.
Quantity of silver contained in the same volume about the cathode after electrolysis . . = 1.3060 grams.
Loss of silver in the volume V of the solution about the cathode . . . . . = 0.1691 gram.

If no silver had come into this portion of the solution about the

cathode by migration, its loss would have been 0.3208 of a gram of silver, the quantity deposited on the cathode, instead of 0.1691 of a gram, the value found. Hence the quantity of silver which migrated to the cathode portion is given by the equation,

$$0.3208 - 0.1671 = 0.1517 \text{ gram.}$$

If as much silver had migrated to the cathode region as had been removed from it by deposition on the cathode, namely, 0.3208 of a gram, then since

$$\text{transference number} = \frac{\text{quantity of the ion migrated}}{\text{quantity of the ion separated}},$$

$$\text{transference number of } Ag^{\cdot} = \frac{0.3208}{0.3208} = 1, \text{ and}$$

$$\text{transfer. number } NO_3' = 1 - \text{transfer. number } Ag^{\cdot} = 0.$$

This would show that, in this case, the NO_3' ions did not share in the migration or in the conduction of the electric current. In Hittorf's experiment, then,

$$\text{transference number } Ag^{\cdot} = \frac{0.1517}{0.3208} = 0.473, \text{ and}$$

$$\text{transference number } NO_3' = 1 - 0.473 = 0.527.$$

As a check on the accuracy of the determination, the change in the concentration of the silver about the anode could be measured. It should be found that the solution about the anode has lost by migration the same quantity which that about the cathode has gained. In the above experiment, for example, it should be found that the loss in silver in the solution about the anode, due to migration away from it, is equal to 0.1517 of a gram, which is identical with the gain in concentration about the cathode also due to migration.

If very exact results are desired, it is advisable to remove sufficiently large portions of anode and cathode solutions, analyse them, and from the results so obtained, to calculate the quantities of the ions which have been transferred.

When the anion can be more easily determined than the cation, its concentration changes may be measured at the anode, or the cathode, or at both the anode and the cathode, quite as well as the concentration change of the cation. This may be illustrated by the determination of the transference numbers of cadmium and chlorine ions. In this case the anode consists of amalgamated cadmium,

which reacts with the chlorine liberated at its surface, forming thereby cadmium chloride. Hence the quantity of chlorine separated may be obtained by determining the loss in weight of the anode during electrolysis. The concentration of the chlorine about the anode before and after the passage of the electric current is determined, and the quantity of chlorine separated at the anode deducted from the latter value. The difference obtained by subtracting from the original concentration the difference between the final concentration and the quantity of separated chlorine is the "loss" suffered by the anode portion. From the total quantity of chlorine separated and from the loss suffered by the anode portion, the quantity of chlorine which migrated is easily calculated, since it is equal to the quantity of chlorine separated diminished by the loss about the anode.

There are a great many forms of apparatus which have been used for the measurement of transference numbers. In order to give an idea of the essential features of such an apparatus, that used by Nernst and Loeb[1] for the determination of the transference numbers of the silver salts is here described. It is shown in Figure 26. In form it resembles a Gay-Lussac burette.

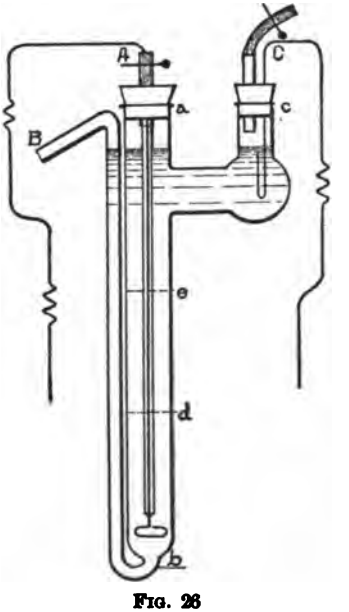


FIG. 26

The two electrodes are of silver. When a current of electricity is passed through the solution, a quantity of silver deposits upon the cathode *C*, which is a measure of the quantity of electricity passed, and the same quantity of silver dissolves from the anode *A*. In order to avoid the disturbance caused by the falling of the silver from the cathode, the latter is placed in a side tube, of the same diameter as the main tube, being introduced as shown in the figure. The cathode consists of a cylindrical piece of silver foil attached to a silver wire. The anode *A*, consisting of a silver wire twisted into a spiral at its lower end and encased by a glass tube throughout its straight portion, is placed in the main tube as shown. The openings

[1] *Ztschr. phys. Chem.*, **2**, 948 (1888).

at *a* and *c* are closed by cork stoppers through which small pieces of glass tubes are passed. The piece of tubing in *a* simply allows the passage of the anode wire, while that in *c* has a piece of platinum wire fused into its side, upon which the cathode hangs. Both tubes may then be closed by means of pieces of rubber tubing and pinchcocks. With this arrangement it is possible to remove portions of the solution from the apparatus, without disturbing the electrodes, by merely blowing at the tube which passes through *c*.

In carrying out an experiment by means of this apparatus, the electrodes together with the corks, without, however, the piece of rubber tubing, are weighed. When the apparatus is again assembled as shown in the figure, with the rubber tube at *a* closed with pinchcocks, and the end of the tube *B* placed in the solution to be investigated, it is filled to a point above the level of the upper side of the side tube by sucking at the rubber tube at *c*. The apparatus usually holds from forty to sixty cubic centimeters. With the exit tube *B* closed with a rubber cap, the whole apparatus is placed in an upright position in a thermostat. After the solution in the apparatus has reached the temperature of the thermostat, the electric current is conducted through the solution. Immediately at the end of the electrolysis, the exit is opened and, by blowing at the tube *c*, the desired quantity of the solution about the anode (from *b* to *d*) is forced out through the tube *B* into a tared flask, weighed and analyzed. The quantity of solution remaining in the apparatus is found by weighing the apparatus and liquid together, and then subtracting from this weight the weight of the apparatus alone. If no considerable mixing of the solution by diffusion or convection currents has occurred during the electrolysis, the portion of the solution about the anode which has undergone a change in concentration is mostly removed with the first few cubic centimeters. The remainder is thoroughly washed out by the unchanged solution which follows it through the tube *B*. The following portion of solution, from *d* to *e*, should then be unchanged in concentration, while the concentration of the solution remaining in the apparatus is changed, since it is from the region about the cathode. A test of the accuracy of the experiment is found in the unaltered condition of the middle portion of the solution *d e*, and also in the fact that the solution about the cathode loses as much silver as that about the anode gains.

In order to guard against a mixing of the solution, many investigators have used diaphragms. It is now known that, while porous porcelain membranes may be used without thereby incurring error,

other membranes, such as animal membranes, influence the value of the transference number. In the case of the latter class, concentration changes take place directly at the two surfaces of the membrane, just as they would if, in place of the membrane or diaphragm, a layer of a solvent, in which the transference numbers of the electrolyte are not the same as they are in the solution, is introduced into the circuit.

At the beginning of his work, Hittorf questioned himself as to the constancy of transference numbers, and further, if they are not constant, as to the circumstances upon which their variation depends. Upon further consideration, he recognized three influences which must be taken into account, namely, that of the current, that of the concentration of the solution, and that of the temperature. He found that the velocities of migration were independent of the current and therefore of the electrical force acting upon the ions, but dependent upon the concentration of the solution.

As solutions of greater and greater dilutions were examined, he found that a point was finally reached beyond which further dilutions caused no appreciable change in the relative velocities of migration. This behavior is easily explained. In the concentrated solutions there are a large number of undissociated molecules, which offer a resistance to the motion of the ions among them which depends upon the nature of the molecules and of the ions. As the dilution becomes greater, this influence gradually disappears, due to an increase in dissociation and to an increase in the distance between the molecules, and a consequent decrease in the resistance offered by them to the motion of the ions. This statement may be applied to mixtures of electrolytes. In this case also the transference numbers of individual ions remain unchanged for moderate concentrations.

Very exact measurements of the influence of concentration on the transference number have recently been carried out by A. A. Noyes,[1] which show that for all the electrolytes investigated, namely,

KCl	HNO_3	K_2SO_4
NaCl	$AgNO_3$	$CuSO_4$
HCl	$Ba(NO_3)_2$	

the transference numbers remain constant within one per cent between the concentrations 0.02 and 0.1 normal. Deviations were only observed in the case of LiCl, $CdSO_4$, and the halogen salts of the divalent metals. These deviations may, as will be made evident

[1] *Technology Quarterly*, 17, No. 4, December, 1904.

later, be explained on the assumption of the formation of double molecules.

Hittorf did not discover any effect produced by such moderate changes in temperature as were involved in his work. Recently, however, Kohlrausch[1] has found that in the case of electrolytes with monatomic univalent ions the transference numbers approach the value 0.50 with increasing temperature. It should be stated here that at the same time the *difference in mobility* of the two ions does not decrease, but actually increases. A numerical example will make these statements clear. Consider that, at the temperature x, the migration velocity of the positive ion is 100, and that of the negative ion is 50; while at a higher temperature y the velocities have become 115 and 60 respectively. The transference number of the positive ion has increased from 0.333 to 0.343. It is evident that the value 0.50 for the transference numbers of the two ions is being approached. At the same time, however, the difference between the single velocities,

$$100 - 50 = 50, \text{ at the temperature } x,$$

and

$$115 - 60 = 55, \text{ at the temperature } y,$$

has increased with rising temperature. Such a simple relation between the temperature and the velocity of migration of the ions is not found in the case of other classes of electrolytes.

The values of the transference numbers obtained with the solvent water do not apply to other solvents. For example, while potassium chloride, bromide, and iodide dissolved in water solution all give the value of the transference number $n_a = 0.51$, when dissolved in phenol they all give the value of $n_a = 0.19$. With this change in the value of the transference numbers, there is a corresponding change in concentration at the boundary surface between the two solvents in which the same electrolyte is dissolved when an electric current passes.[2]

Still another advance was made possible by Hittorf's study of the concentration changes at the electrodes, namely, the discovery of the composition of the ions resulting from the dissociation of compounds. Silver cyanide, for example, dissolves in potassium cyanide,

[1] Sitzungsber. d. königl. Pr. Akademie d. Wiss. Physik. Mathem. Kl., **26**, 572 (1902).

[2] Nernst and Riesenfeld, *Drud. Ann.*, **8**, 600 and 609 (1902). For transference numbers in mixed solvents see Jones and Basset, *Chem. Centrbl.*, 1905, I, 71. A collection of references to the literature is given by Walden, *Ztschr. phys. Chem.*, **46**, 103 (1902).

forming a compound which in the solid state has the composition represented by the formula $AgCN \cdot KCN$. From this fact alone, however, it is not possible to state what ions this compound forms upon dissociation in aqueous solution. Now Hittorf passed an electric current through such a solution and found that silver was deposited upon the cathode. He determined further the concentration of potassium and of silver about the cathode before and after the electrolysis, and found that, including the silver deposit, an increase in the potassium concentration above that of the silver had taken place, corresponding to the quantity of electricity passed through the solution. These results contradict the assumption that both the silver and potassium are present in solution as positive ions. Hittorf interpreted the results in the following manner: The potassium forms positive ions, while the silver and the cyanide radical unite and form negative ions. In solution, then, this salt would be represented by the formula $K^{\cdot}Ag(CN)_2'$. Leaving out of account the quantity of separated substance, the positive and negative ions must always be present in equivalent amounts, which evidently requires that before the electrolysis has taken place the solution contain equivalent quantities of potassium and silver. The potassium separated at the cathode immediately reacts with water, forming potassium hydroxide, thus explaining the presence of an extra quantity of potassium about the cathode corresponding to the quantity of electricity passed through the solution. The separation of silver is then a secondary reaction, caused by the action of the separated potassium, and resulting in the appearance of a double quantity of CN' ions in the place of decomposed $Ag(CN)_2'$ ions.

In a similar manner Hittorf investigated the constitution of other double salts in aqueous solution. He found that they dissociate as shown in the following table: —

Symbol of Solid Salt	Ions in Aqueous Solution
Na_2PtCl_6	$2\,Na^{\cdot} + PtCl_6''$
$NaAuCl_4$	$Na^{\cdot} + AuCl_4'$
$K_4Fe(CN)_6$	$4\,K^{\cdot} + Fe(CN)_6''''$
$K_3Fe(CN)_6$	$3\,K^{\cdot} + Fe(CN)_6'''$

It is even more simple to determine whether a given metal exists in the positive or in the negative ion by a study of the concentration changes which take place about the anode during electrolysis. Since at this electrode no deposition of a metal takes place, then, if the anion is not decomposed at the electrode, the solution about it

will become more concentrated in respect to this ion. If the metal in question is a part of the anion, the solution about the anode will, evidently, become more concentrated in respect to it also. On the other hand, if it forms the cation, it will migrate away from the anode, thus decreasing its concentration in the solution about this electrode. Strictly speaking, when a metal does form a part of an anion, a certain quantity of the metal, even though it be an extremely small part, exists in solution in the form of cations. It can happen, moreover, that the concentration of the solution about the anode does not undergo a change in respect to the metal during electrolysis. This is the case when the change in concentration due to the migration of some of the metal as a part of the anion is exactly compensated by the migration of the rest of it as the cation in the opposite direction.

The constitution of salts which form more than two ions in aqueous solution may also be determined by means of transference numbers.[1] For example, barium chloride may dissociate in two stages according to the following equations: —

$$BaCl_2 \rightleftarrows BaCl^{\cdot} + Cl';$$
$$BaCl^{\cdot} \rightleftarrows Ba^{\cdot\cdot} + Cl'.$$

If it is assumed, accordingly, that, in moderately concentrated solutions, the intermediate complex ion $BaCl^{\cdot}$ exists, which on further dilution breaks down, then the transference numbers, which are obtained from a series of solutions of different concentrations, will differ considerably from one another. With increasing dilution, the value of the transference numbers should decrease, since then the quantity of chlorine carried along with the barium in the ion $BaCl^{\cdot}$ to the cathode is decreased, and since this carrying along of chlorine tends to increase the transference number of the barium and to decrease that of the chlorine. As a matter of fact, however, it was found that the transference numbers varied in the opposite direction from that expected on the above assumption. Therefore it is concluded that in moderately concentrated solutions, one or more mols of undissociated $BaCl_2$ combine with Cl', forming such complex ions as $BaCl_3'$ or $BaCl_4''$, which on further dilution break down again. Whether or not the dissociation in stages also takes place is not known.

It has been suggested by Nernst[2] that it would be possible to obtain light on the question of hydrated ions by means of migration experiments. For instance, if the positive ion migrates with a

[1] A. A. Noyes, *Ztschr. phys. Chem.*, **36**, 63 (1901).
[2] *Jahrb. d. Elektrochemie*, **7**, 70 (1901).

certain number of water molecules while the negative ion migrates with a *different* number, then during the electrolysis water is transferred from one electrode to the other, causing a corresponding change in concentration of an indifferent, non-conducting dissolved substance, the so-called indicator. As is evident, this method gives only the *difference* of the quantities of water carried by the two ions. The preliminary results obtained thus far indicate that the anions of strong mineral acids are hydrated.

Exact experiments with a solution of silver nitrate in aqueous methyl alcohol have recently been made by Lobry de Bruyn.[1] He was unable to detect a change in the concentration of the water or alcohol, and consequently was unable to show either the formation of ion-hydrates or of ion-alcoholates. Morgan and Kanolt,[2] however, found that during the electrolysis of a solution of silver nitrate in water and pyridine a decrease in the concentration of the pyridine took place about the anode. From this it would be concluded that the pyridine combines with the silver ions.

The interpretation of his results given by Hittorf when first published met with great opposition, but are now accepted as correct. They are also now confirmed by the independent results obtained by determinations of the freezing-point lowering of solutions.

It is very interesting to note that there are substances, the so-called *amphoteric electrolytes*,[3] which may dissociate in different ways. Lead hydroxide, $Pb(OH)_2$, for example, may dissociate as follows:—

$$Pb(OH)_2 = PbOH^{\cdot} + OH';$$
$$Pb(OH)_2 = Pb^{\cdot\cdot} + 2\,OH';$$
$$Pb(OH)_2 = H^{\cdot} + PbO(OH)';$$

or finally,

$$Pb(OH)_2 = 2\,H^{\cdot} + PbO_2.$$

In pure water all of these ions exist together in greater or less quantities according to the respective degrees of dissociation. If the first two modes of dissociation predominate, the solution reacts alkaline; if the latter two, it reacts acid. If a strong acid be added to the solution, nearly all of the OH ions combine with the H ions of the acid, forming undissociated water. The reëstablishment of the equilibrium then requires the further dissociation of the undissociated or solid hydroxide into $Pb^{\cdot\cdot}$ and $2\,OH'$. As before, the OH ions are removed by the action of the added acid and the end condition is

[1] *Jahrb. d. Elektrochemie*, 10, 260 (1904).

[2] *Ztschr. phys. Chem.*, 48, 365 (1904).

[3] Bredig, *Ztschr. Elektrochem.*, 6, 33 (1899); *Ztschr. anorg. Chem.*, 34, 202 (1903); Walker, *Ztschr. phys. Chem.*, 49, 82 (1904).

reached that in acid solution divalent lead ions are present almost exclusively. These ions may combine partially with the anions of the acid to form an undissociated salt, or they may form some such complex ions as exist in the case of barium chloride.

If a strong base be added to the solution, the OH ions remove the H ions which were present, and we see at once that in an alkaline solution of lead hydroxide the PbO_2 ions will predominate.

The hydroxides of other metals dissociate similarly. Hydroxides of the alkalies dissociate exclusively into positive metal ions and OH ions.

From what has been said it is evident that the metal in solutions of such amphoteric electrolytes must migrate as cations to the cathode in acid solution and as anions to the anode in alkaline solution.

Lead salts have been found to behave in this way. To be sure, the fact must also be taken into consideration that colloids may migrate with or against the electric current (see chapter on electrical endosmose). Hence the presence of a metallic oxide as an anion in an alkaline solution is not conclusively shown by a migration experiment alone.

From a theoretical standpoint all ions which are possible in a given solution must be present. However, only those whose existence may be detected will receive consideration here. It is objectionable to deal with ions which cannot be detected.

There is a special class of amphoteric electrolytes which form ions which possess a *double nature*, being at the same time acid and basic. Glycocoll furnishes an example of such an ion. It dissociates according to the equilibrium equation,

$$HOH_3NCH_2COOH \rightleftarrows \underline{H_3NCH_2COO'} + H' + OH'.$$

The ion underlined is charged both positively and negatively, and hence is electrically neutral, taking no part in migration and in the conduction of the electric current.

Another experiment concerning the electrolysis of mixtures of electrolytes which was performed by Hittorf may well be mentioned here. He found, in his study of solutions of potassium chloride and of potassium iodide, that the chlorine and iodine ions migrate with very nearly the same velocity. With our present knowledge, it may be predicted with great certainty that during the electrolysis of a mixture of these salts, the ratio of the concentrations of the chlorine to that of the iodine will not change, since the chlorine and iodine ions take part equally in the conduction of the

electric current. Such was actually found to be the case. At that time, the fact that when such a solution of these two salts was electrolyzed iodine alone separates at the anode, caused much trouble, since the phenomenon of electrical conduction was not distinguished from that of electrolytic decomposition. It was concluded that possibly the iodine alone, belonging to a more easily decomposed compound, conducted the current. The fact that iodine alone separates at the anode has nothing to do with the phenomenon of conduction. In the chapter on polarization this subject will be again considered.

Recently, the question as to whether the lines of current, or the ions migrating from one electrode to another, may be diverted from their paths by electro-magnetic action, has received attention,[1] negative results being obtained.

Up to the present but few transference experiments have been carried out with fused electrolytes.[2]

It is natural that the important phenomenon of migration should play an important part in commercial processes. In the electrolysis of concentrated solutions of potassium chloride on a large scale in a vessel divided into two parts by means of a porous diaphragm, alkali is produced at the cathode and chlorine at the anode. The latter is evolved and collected, while the alkali accumulates in the cathode section. Consequently the alkali thus formed takes part in the conduction, by the migration of hydroxyl with the chlorine ions toward the anode, thus decreasing the yield of alkali. This decrease becomes greater the greater its concentration in the cathode section. For this reason in the works the concentration of alkali is not allowed to exceed six or eight per cent. It should especially be remarked that, with an increase in temperature, not only is the conductivity of the solution increased, but also the yield in alkali is increased, since the transference numbers of electrolytes having univalent ions thereby approach the value 0.5.

It seemed surprising, at first, that the alkali yield in the electrolysis of a potassium chloride solution is about ten per cent higher than that in the electrolysis of a sodium chloride solution under the same conditions. A consideration of the transference numbers in the two cases, however, explains the phenomenon. The transference number of OH' at 18° in 1/1 normal solution of potassium hydroxide is 0.74, while in a 1/1 normal solution of sodium hydroxide it is 0.825. Thus, in the former solution fewer OH ions migrate toward the anode when a given quantity of alkali is formed at the

[1] Heilbrun, *Drud. Ann.*, 15, 988 (1904).

[2] Lorenz and Fausti, *Ztschr. Elektrochem.*, 10, 620 (1904).

cathode than in the latter solution, since the migration velocity of the potassium ion is greater than that of the sodium ion. The yield may also be increased by conducting a stream of carbon dioxide through the alkali at the cathode. The rapid ion OH' is thereby replaced by the slower ion CO_3''. To be sure, it must in this case also be recognized that the product obtained, the carbonate, is of less value than the hydroxide.

If a current of the solution is made to flow, with the velocity with which the hydroxide ions migrate, from the anode to the cathode, the loss in alkali is decreased. In the production of alkali, it is only necessary to have a conveniently formed apparatus, without a diaphragm, through which a salt solution may be allowed to flow from the anode to the cathode, in order to obtain a quantitative yield. Since, however, the migration velocity of the OH ions is considerable, it would be expected that only a dilute solution of alkali could be obtained when the electric current is well utilized. Nevertheless, it is possible to obtain a fifteen per cent solution of alkali with a ninety per cent utilization of the electric current, in this way. The chief cause of this good yield must be sought in another direction. It is found in the stream of concentrated salt solution which is allowed to flow into the apparatus at the anode. The OH ions, migrating toward the anode, then pass from layers of solution which are dilute in respect to the Cl ions to those which are concentrated, and, consequently, take part less and less in the conduction of the electric current. The progress of the OH ions toward the anode is, in this way, checked more and more as the anode is neared. The so-called bell process is based upon these principles.[1]

A yield of alkali which is almost quantitative may also be obtained by the electrolysis of chloride solutions, using a mercury cathode. In this way the formation of OH ions is prevented, since under the influence of the electric current an alkali amalgam is formed. Care must, of course, be taken to constantly replace the amalgam with pure mercury. The former is transferred to a second vessel containing water, where it is decomposed, forming alkali and mercury. This so-called mercury process is carried out in various modified forms.[2] It possesses the advantage that by means of it very concentrated lye, which is free from salt and which can be used directly in the industries, is produced. The lye obtained by the

[1] Adolph, *Ztschr. Elektrochem.*, 7, 581 (1901); Steiner, *Ztschr. Elektrochem.*, 10, 317 (1904).

[2] F. Glaser, *Ztschr. Elektrochem.*, 8, 522 (1902); Kettembeil-Carrier, *Ztschr. Elektrochem.*, 10, 561 (1908); Le Blanc-Cantoni, *Ztschr. Elektrochem.*, 11, 609 (1905).

bell or diaphragm processes must be concentrated by evaporation and purified by removing the salts before being used.

In many cases it is possible to avoid the damaging effects of migration in a more rational manner. In the dye works, a solution of chromic acid in sulfuric acid is generally used as an oxidizing agent. During the oxidation, the chromic acid is transformed into chromium sulfate. The chromic acid can then be regenerated, electrolytically, by placing the chromium sulfate solution in the anode section of an electrolytic cell, which is provided with a diaphragm, and sulfuric acid in the cathode section, and passing an electric current through the cell. During the electrolysis, SO_4 ions migrate from the cathode section into the anode section, thereby enriching the sulfuric acid in the latter section at the expense of the acid in the cathode section. In such a process it is necessary to precipitate the excess of sulfuric acid in the chromic acid solution from time to time with lime, and to replace, with concentrated sulfuric acid, the diluted and impure acid of the cathode section. This may, however, be avoided by first placing the chromic acid solution in the cathode section, in place of the pure sulfuric acid, and passing an electric current long enough to sufficiently oxidize the corresponding liquid in the anode section. This anode liquid is used directly in the works, whereby chromium oxide is again formed, and is then allowed to flow into the cathode section, where it is again electrolyzed. The solution used in the previous electrolysis in the cathode section, is, this time, used in the anode section. Before the second electrolysis, the cathode solution is richer in sulfuric acid than the anode solution, but during it this excess migrates to the latter solution. A cyclical process is thus carried out, in which the chromic acid solution is alternately placed in the anode and cathode sections, thus preventing the accumulation of an excess of sulfuric acid in it, and making it possible to maintain the solution at a given concentration during its regeneration by electrolysis. By means of such a process, a solution of chromic acid in sulfuric acid may be used as an oxygen carrier as long as desired without loss of either chromic or sulfuric acid.[1]

A table of the transference numbers of the ions of the most important and best-investigated electrolytes is given on the next page. The values have been taken from Kohlrausch and Holborn's "Das Leitvermogen der Elektrolyte," and from the recent works of Noyes,[2] Jahn,[3] and Tower.[4]

[1] Le Blanc, *Ztschr. Elektrochem.*, 7, 290 (1900).

[2] *Ztschr. Phys. Chem.*, 36, 63 (1901).

[3] *Ztschr. Phys. Chem.*, 37, 673 (1901).

[4] *J. Am. Chem. Soc.*, 26, 1039 (1904).

TRANSFERENCE NUMBERS OF ANIONS (n_a)

For solutions containing m equivalents of the respective substances per liter of water, or, in other words, for solutions containing one equivalent in D liters of water (at about 18° t). Doubtful values are given in small type.

	m =	0.01	0.02	0.05	0.1	0.2	0.5	1	1.5	2	3	5	7	10
K{Cl, Br, J}, NH_4Cl		0.503	0.503	0.503	—	—	—	—	—	—	—	—	—	—
NaBr, NaCl		0.604	0.604	0.604	—	—	—	—	—	—	—	—	—	—
LiCl		0.670	0.670	0.680	0.687	0.697	—	—	—	—	—	—	—	—
KNO_3		—	—	—	0.497	0.496	0.492	0.487	0.482	0.479	—	—	—	—
$NaNO_3$		—	—	—	0.615	0.614	0.612	0.611	0.610	0.608	0.603	0.585	—	—
$AgNO_3$		0.528	0.528	0.528	0.528	0.527	0.519	0.501	0.487	0.476	—	—	—	—
$KC_2H_3O_2$		—	—	—	0.33	0.33	0.33	0.331	0.332	0.332	0.333	0.335	—	—
$NaC_2H_3O_2$		—	—	—	0.44	0.43	0.43	0.425	0.422	0.421	0.417	—	—	—
KOH		—	—	—	0.735	0.736	0.738	0.740	—	—	—	—	—	—
NaOH		—	—	0.81	0.82	0.82	0.82	0.825	—	—	—	—	—	—
LiOH		—	—	—	0.85	0.85	0.861	0.878	0.890	—	—	—	—	—
HCl		0.174	0.174	0.174	—	—	—	—	—	—	—	—	—	—
HNO_3		0.170	0.170	0.170	0.170	0.170	—	—	—	—	—	—	—	—
½ $BaCl_2$ at 25°		—	—	0.558	—	0.585	—	—	—	—	—	—	—	—
½ $CaCl_2$		0.58	0.59	0.61	0.64	0.66	0.675	0.686	0.695	0.700	0.710	0.737	0.764	0.79
½ $MgCl_2$		—	—	0.63	0.66	0.68	0.69	0.709	0.718	0.729	0.747	0.776	0.799	—
½ $CdCl_2$		0.570	0.570	0.570	0.570	0.65	0.69	0.72	0.73	0.745	0.767	0.865	0.995	—
½ CdJ_2		0.558	0.554	0.606	0.69	0.86	1.00	—	—	—	—	—	—	—
½ $Ba(NO_3)_2$ at 25°		—	—	0.544	—	0.545	—	—	—	—	—	—	—	—
½ K_2SO_4 at 25°		—	—	0.504	—	0.507	—	—	—	—	—	—	—	—
½ K_2CO_3		—	—	0.39	0.40	0.41	0.435	0.434	0.421	0.413	0.404	0.380	0.365	—
½ Na_2CO_3		—	—	0.52	0.56	0.58	0.54	0.548	0.546	0.542	0.530	—	—	—
½ $MgSO_4$		—	—	0.60	0.64	0.66	0.70	0.74	0.75	0.76	0.760	—	—	—
½ $CuSO_4$		—	0.625	0.625	0.626	0.657	0.672	—	—	—	—	—	—	—
½ H_2SO_4		—	0.177	0.177	0.177	0.177	—	—	—	—	—	—	—	—
	D =	100	50	20	10	5	2	1	0.66	0.5	0.33	0.2	0.14	0.1

CHAPTER V

THE CONDUCTANCE OF ELECTROLYTES

Specific and Equivalent Conductance. — The conception of resistance in the case of conductors of the first class has already been discussed. The resistance of such conductors is dependent upon the nature of the material of which they are formed, their form, and their temperature. If, for a cylinder one centimeter in length and one square centimeter in cross section, of a certain substance,

$$R, \text{ the resistance} = \frac{1}{K},$$

then for any cylindrical piece of the same substance at the same temperature,

$$R = \frac{1}{K} \times \frac{l}{s}$$

when l represents the length of the cylinder in centimeters and s its cross section in square centimeters. The factor $\frac{1}{K}$ represents the *specific resistance* of the substance. It depends only on the temperature.

The unit of resistance is the *ohm*. It is the resistance of a conductor in which a current of one ampere flows when a difference of potential of one volt exists between the ends of the conductor. A substance which in the form of a cylinder one centimeter in length and one square centimeter in cross section possesses a resistance of one ohm represents a unit of resistance. For it $\frac{1}{K} = 1$. In practice, however, the unit of resistance is represented by the resistance of a column of mercury, 106.3 centimeters in height and one square millimeter in cross section, at the temperature of melting ice. The mass of this column of mercury must be 14.4521 grams.

Formerly, the unit of resistance was defined to be the resistance of a column of mercury, one meter in length and one square millimeter in cross section at 0° t. This unit is known as the Siemens or mercury unit. It is related to the new unit as 1 : 1.063, and there-

fore, in order to calculate the resistance in ohms from a resistance expressed in Siemens units, or conversely, the following equation may be used:—

Resistance in ohms = Resistance in Siemens units ÷ 1.063.

In the following pages, the ohm is used as the unit of resistance.

The greater the resistance, the less the conductance; and, conversely, the greater the conductance, the less the resistance. Hence, the resistance R and the conductance K are reciprocal quantities, or

$$R = \frac{1}{K}.$$

The word *conductance* is used mainly with reference to solutions, and in the following pages will be used only with such a reference. Just as in the case of conductors of the first class, the unit of specific conductance, which may be expressed in reciprocal ohms, could be represented by the conductance of a cylinder of a liquid, one centimeter in height and one square centimeter in cross section, which possesses a resistance of one ohm. For such a liquid $\underline{K} = 1$. Furthermore, the same law which expresses the variation of the resistance of a conductor at constant temperature with a variation of its dimensions applies also to conductors of the second class. That is,

$$K = \frac{1}{R} = \underline{K} \times \frac{s}{l},$$

where K is the conductance, $\underline{K}$ the specific conductance, or conductivity, R the resistance, s the cross section, and l the length of the liquid conductor. This method of expressing conductance has not, however, been found suitable for obtaining numerical relationships between solutions. Since electro-chemistry deals chiefly with solutions, it has been found advisable to adopt a special method of expressing their conductances. In the case of solutions, the conductance depends almost entirely upon the solute, or the dissolved substance, and in comparing their conductances, it has been found advantageous to refer the conductances to a certain quantity of solute, namely, one equivalent weight, rather than to any particular volume of solution. The conductance of a solution containing one equivalent of the solute, when placed between parallel electrodes one centimeter apart, is called its *equivalent conductance* $\underline{K}$.

If C'_e represents the equivalent concentration of a solution, *i.e.* the concentration expressed in equivalents of the solute per cubic centimeter of solution, then

$$D'_e = \frac{1}{C'_e},$$

where D'_e represents the equivalent dilution of the solution, or in other words, the volume in cubic centimeters which contains one equivalent of the solute. Accordingly,

$$\underline{\underline{\kappa}} = \frac{\kappa}{C'_e} = \kappa D'_e.$$

The relation between the equivalent conductance $\underline{\underline{\kappa}}$ and the specific conductance κ is reached as follows: [Consider a vessel, such as is shown in Figure 27, constructed of two non-corrodible metallic plates A and C, serving as electrodes, which are held at a distance of one centimeter from each other by the nonconducting material which forms the ends and bottom of the vessel.]

One cubic centimeter of a solution containing one equivalent of a solute is placed in this vessel, reaching to the level a. The cross section of the solution, perpendicular to the direction of the electric current between the two electrodes, is then one square centimeter. The equivalent concentration of this solution is unity, and hence its dilution is also unity. Since its volume is one cubic centimeter and it is placed between electrodes one centimeter apart, its conductance is directly the specific conductance or conductivity, and since it contains one equivalent weight of dissolved substance placed between electrodes one centimeter apart, its conductance is also the equivalent conductance. These facts concerning this solution may also be expressed by the following equations: —

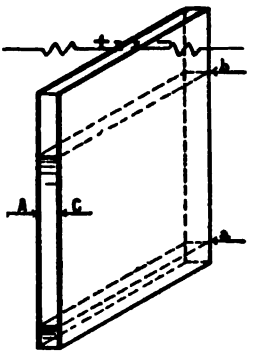


FIG. 27

$$C'_e = 1,\ D'_e = 1,\ \text{and}\ \kappa = \underline{\kappa} = \underline{\underline{\kappa}}.$$

If, however, the volume of the above solution be increased to one thousand cubic centimeters by the addition of water, thereby reaching the new level b, the cross section of this solution is one thousand times as great as that of the original solution, or one thousand square centimeters. But the conductance of a quantity of this solution having a cross section of one square centimeter is the specific conductance, or the conductivity of the solution. Hence the actual conductance of this solution is one thousand times as great as the specific conductance, or conductivity. The solution still contains one equivalent of the dissolved substance between the electrodes, and therefore the actual conductance is still identical with the

equivalent conductance, this time at the dilution, 1000. It may be said, in general, that whenever one equivalent of a substance in aqueous solution, of any concentration or dilution, is placed in such a vessel, its actual conductance is equal to the equivalent conductance at the concentration in question. It follows from what has been stated, that in the above case the equivalent conductance of the solution is also one thousand times as great as its conductivity. These relations are expressed by the following equations: —

$$\kappa = \underline{\kappa} = 1000\,\underline{\kappa} = D'_e\kappa = \frac{\kappa}{C'_e}.$$

The specific conductance, or conductivity, of a solution changes nearly in proportion to the concentration, while the equivalent conductance generally increases rapidly at first, then more slowly, and finally remains constant, with decreasing concentration. This will be evident from a study of the table of equivalent conductances of salts, acids, and bases in aqueous solution at different concentrations, given here. This table contains among other results the most recent ones obtained by Kohlrausch.

EQUIVALENT CONDUCTANCES AT 18° *t*

C_e equivalent concentration[1]	KCl	NaCl	KNO_3	$AgNO_3$	$\frac{1}{2}CuSO_4$	$\frac{1}{2}H_2SO_4$	HCl	CH_3COOH	KOH	NH_3	D_e equivalent dilution[2]
0.0001	129.07	108.10	125.50	115.01	109.95	—	—	107	—	(66)	10 000
0.0002	128.77	107.82	125.18	114.56	107.90	—	—	90	—	58	5 000
0.0005	128.11	107.18	124.44	113.88	103.56	(368)	—	57	—	38.0	2 000
0.001	127.34	106.49	123.65	113.14	98.56	361	(377)	41	(284)	28.0	1 000
0.002	126.31	105.55	122.60	112.07	91.94	351	376	30.2	(233)	20.6	500
0.005	124.41	103.78	120.47	110.06	80.98	330	373	20.0	230	13.2	200
0.01	122.43	101.95	118.19	107.80	71.74	308	370	14.3	228	9.6	100
0.02	119.96	99.62	115.21	—	62.40	286	367	10.4	225	7.1	50
0.05	115.75	95.71	109.86	99.50	51.16	258	360	6.48	219	4.6	20
0.1	112.08	92.02	104.79	94.33	43.85	225	351	4.60	213	3.3	10
0.2	107.96	87.78	98 74	—	37.66	214	342	3.24	206	2.30	5
0.5	102.41	80.94	89.24	77.5	—	205	327	2.01	197	1.35	2
1	98.27	74.85	80.46	67.6	25.77	198	301	1.32	184	0.89	1
2	92.6	64.8	69.4	—	—	188.0	254	0.80	160.8	0.582	0.5
3	88.3	56.5	(61.3)	—	—	166.8	215.0	0.54	140.6	0.364	0.33
5	—	42.7	—	—	—	135.0	152.2	0.335	105.8	0.202	0.2

[1] Equivalent concentration, $C_e = \frac{\text{Equivalents}}{\text{Liters}}$.

[2] Equivalent dilution, $D_e = \frac{\text{Liters}}{\text{Equivalents}}$.

General Regularities. — The first clear conceptions concerning the conductance of electrolytes resulted from the epoch-making work of Kohlrausch. The work of discovery was then rapidly pushed forward by Arrhenius, Ostwald, and others. It was found that, without exception, the equivalent conductance of different electrolytes increases with increasing dilution, reaching in many cases a maximum value which does not change upon further dilution. The following statement, called Kohlrausch's principle,[1] has been found to hold for solutions which have been diluted until the maximum equivalent conductance has been reached: —

The equivalent conductance of a binary electrolyte is equal to the sum of two values, one of which depends upon the cation, and the other upon the anion.

This principle expresses the fact that the conductance of an electrolyte is equal to the sum of the conductances of its ions. Because of this fact the conductance of an electrolyte is called an *additive property.* The principle is evident from a study of the following table,[2] in which the equivalent conductances, at great dilutions of several series of salts, are given. For example, in the first horizontal row are given the values for KCl, NaCl, TlCl, and LiCl, and the differences between these values; while in the first column are given the equivalent conductances of KCl, KNO_3, KF, and $KC_2H_3O_2$, and also the differences between these values. The differences in each case are printed in small type.

	K	diff.	Na	diff.	Tl	diff.	Li
Cl	129.1	21.0	108.1	22.2	130.3	22.2	98.1
diff. =	3.6	—	3.5	—	3.7	—	3.6
NO_3	125.5	20.9	104.6	22.0	126.6	22.1	94.5
diff. =	15.0	—	15.2	—	12.2	—	—
F	110.5	21.1	89.4	25.0	114.4	—	—
diff. =	10.5	—	12.6	—	—	—	—
$C_2H_3O_2$	100.0	22.2	76.8	—	—	—	—

If now the differences in the rows and in the columns be considered, it is seen that they are nearly constant for any given row or column. Such a relation is possible only when the values of the conductances are made up of two independent constants. A great many other properties of *dilute* solutions of electrolytes are known which may similarly be considered as the average of the properties of the

[1] *Wied. Ann.*, 6, 1 (1879), and 26, 213 (1885).

[2] Temperature = 18° t; equivalent dilution = 10^7 c.cm.

ions constituting the electrolyte. Such properties are called *additive properties*. As further examples of such properties of solutions, may be mentioned the color and the index of refraction.

It will be seen that the dissociation theory offers a ready explanation for the above experimentally found regularities. The conduction of electricity through a solution consists in the motion of single ions. If, when a solution containing x ions is placed in an electric circuit, 100 ions pass through a cross section of the solution in a given time, then, if the number of ions be increased to $2x$, other conditions remaining constant, 200 ions will pass through a cross section in the same time. In other words, *when the number of ions in a given solution is doubled, the conductance of the solution is also doubled.*

As has already been indicated, the equivalent conductance of a binary electrolyte can be measured directly by placing a solution containing one equivalent of it in a vessel, such as is shown in Figure 27, two of whose walls (exactly one centimeter apart) serve as electrodes. Other dimensions of the vessel than the distance between the wall-electrodes need not be fixed. The actual conductance measured is then the equivalent conductance. As long as one equivalent of the electrolyte is in solution between the electrodes, this is always the case, whatever the volume of the solution may be. When the electrolyte is completely dissociated, its solution contains one equivalent of anions and one of cations. Its equivalent conductance, then, remains constant, whatever the dilution, since the same number of ions is always present, and since it is by means of these ions alone that the conduction takes place. The conductance of the electrolyte is independent of the size of the electrodes, providing a change in size is not accompanied by either an increase or a decrease in the number of ions in the solution. Hence it is possible to extend the wall-electrodes to any desired size, without thereby affecting the conductance of a given solution placed between them, and thus to measure the equivalent conductance directly at such great dilutions that its value finally remains practically constant. From what has been said it is easy to understand why the equivalent conductance of a concentrated solution is less than that of a dilute solution. In the former case, since more molecules remain undissociate than in the latter case, it follows that fewer ions per equivalent of electrolyte are present to conduct the electric current. Hence it may be stated —

With increasing dilution the degree of dissociation, and consequently also the equivalent conductance, of an electrolyte increases, until complete

dissociation and the corresponding, or maximum, value of the equivalent conductance is reached.

The requirement of the dissociation theory that upon dilution the equivalent conductance should increase, reaching a maximum constant value at great dilutions, is in complete agreement with facts. According to the Clausius theory, however, the conductivity depends upon the frequency of the changes which take place between the positive and negative parts of the molecules. It is, therefore, a natural conclusion from this theory that the more concentrated the solution, the more often will these changes take place, and, consequently, the greater will be the equivalent conductance. This, however, is in direct contradiction to facts. The superiority of the dissociation theory over the Clausius theory is, in this case, at once evident.

The conductance of a solution depends not only upon the number of ions which exists between the two electrodes, but also upon the sum of their velocities of migration. Since dilute equivalent solutions of neutral salts, strong acids, and strong bases are practically completely dissociated, they contain the same number of ions, and consequently their equivalent conductances are to each other as the sums of the migration velocities of their respective ions. Since an ion is free to move independently of other ions present in the solution, it possesses an independent and constant velocity of migration. It follows then that the equivalent conductance may be expressed in terms of the sum of the migration velocities of the ions involved and a constant which depends upon the units chosen, as follows: —

$$\Lambda = \text{constant} \times (v_a + v_c),$$

where v_a and v_c represent the migration velocities of one equivalent of positive and negative ions, respectively (see page 70). This is an expression of the *Law of Kohlrausch.*

The sum of the migration velocities may therefore be obtained from the maximum value of the equivalent conductance. The relation between the single migration velocities, or the relative migration velocity, is known from Hittorf's work. Therefore the single values may be calculated.

$$\Lambda = \text{const.}\ (v_a + v_c);$$

$$n_a = \frac{v_a}{v_c + v_a};$$

$$n_a\Lambda = \text{const.} \times v_a,$$

or

$$v_a = \frac{n_a\Lambda}{\text{const.}};$$

and $$(1 - n_a)\Lambda = \text{const.} \times v_c,$$

or $$v_c = \frac{(1 - n_a)\Lambda}{\text{const.}}.$$

If the migration velocities are expressed in the same units as the conductances, then the constant becomes unity. The above equations may be written as follows: —

$$v_a = n_a\Lambda, \quad \text{and} \quad v_c = (1 - n_a)\Lambda.$$

When the value of the velocity of migration of a given ion is once determined, that of the others may be calculated either from transference numbers or relative migration velocities, or from the maximum values of the equivalent conductances, whenever these are known. Kohlrausch has calculated and compared many of these migration velocities and found that the two methods of determination give the same results. This agreement of results obtained from two sources is a strong confirmation of the correctness of the present conceptions of electrolysis.

The following illustrative example will make the method of calculation clearer.

The maximum value of the equivalent conductance Λ_∞, or the value at infinite dilution, of potassium chloride was found by a method of extrapolation to be 129.9. The transference numbers in a very dilute solution of the salt were found to be —

$$n_a = 0.503 \quad \text{and} \quad 1 - n_a = 0.497;$$

but $v_a = n_a\Lambda_\infty, \qquad v_c = 1 - n_a\Lambda_\infty,$

or $v_a = 0.503 \times 129.9, \qquad v_c = 0.697 \times 129.9;$

$v_a = 65.3, \qquad v_c = 64.6.$

The corresponding equivalent conductance of sodium chloride was found to be 108.9. The value of v_{cl}, or the migration velocity of chlorine, was found in the preceding paragraph to be 65.3. Hence, since

$$\Lambda_\infty = v_a + v_{cl},$$

$$v_c = 108.8 - 65.3 = 43.6 \text{ for sodium.}$$

The transference numbers in a sodium chloride solution were found to be —

$$n_a = 0.604, \qquad 1 - n_a = 0.396;$$

but $$n_a = \frac{v_a}{v_a + v_c};$$

or, since $v_a = 65.3$, $v_c = \frac{65.3}{0.604} - 65.3 = 42.8$ for sodium.

These two values for the migration velocity of sodium agree satisfactorily with each other.

The following values of the migration velocity, at infinite dilution, at 18° *t*, are taken from those collected by Kohlrausch:[1] —

CATIONS				ANIONS			
CATION	u_c	CATIONS	u_c	ANION	u_a	ANIONS	u_a
H	318.	½ Ba	55.10	OH	174.	CHO_2	46.7
K	64.87	½ Sr	51.54	Fl	46.64	$C_2H_3O_2$	35.0
Na	43.55	½ Ca	51.46	Cl	65.44	$C_3H_5O_2$	31.0
Li	33.44	½ Mg	45.94	Br	67.63	$C_4H_7O_2$	27.6
Rb	67.6	½ Zn	46.57	I	66.40	$C_5H_9O_2$	25.7
Cs	68.2	½ Cd	47.35	SCN	56.63	$C_6H_{11}O_2$	24.3
NH_4	64.4	½ Cu	47.16	ClO_3	55.03	½ $(COO)_2$	62.6
Tl	66.00	½ Pb	61.10	BrO_3	46.2	½ SO_4	68.14
Ag	54.02			IO_3	33.87	½ CrO_4	72.0
				NO_3	61.78	½ CO_3	60.0
				ClO_4	64.7		
				IO_4	47.7		
				MnO_4	53.4		

Further values are given in the section on the migration velocity of individual ions (see page 116). The corresponding values for other temperatures may be calculated with the aid of the temperature coefficient given later in this chapter.

The conductance at great dilution is expressed by the equation,

$$\Lambda_\infty = u_c + u_a.$$

In this case the dissociation is complete. If, on the other hand, at any other dilution *D* only a part of the molecules is dissociated, then the conductance is less. For example, if at this dilution but one half of the total number of molecules are dissociated, the conductance is but one half its value at infinite dilution. This is expressed by the equation,

$$\Lambda_D = \tfrac{1}{2}(\Lambda_\infty) = \tfrac{1}{2}(u_c + u_a).$$

[1] Sitzungsber. d. K. Pr. Akad. d. Wiss. Physik. Math. Kl., 574 and 582 (1902), and also in the number dated July 28, 1904. (Abstracted in *Ztschr. phys. Chem.*, **51**, 744, 1905).

The value for $H^{\cdot}$ has been confirmed by the recent work of Goodwin and Haskell, Proc. Am. Acad. of Arts and Sci., Vol. 40, No. 7 (September, 1904).

The value for CO_3'' has been taken from the investigation of Böttger, *Ztschr. phys. Chem.*, **46**, 594 (1903).

An attempt to explain the strikingly great mobility of $H^{\cdot}$ and OH' has been given by Danneel, *Ztschr. Elektrochem.*, **11**, 249 (1905).

In deriving this equation, it was tacitly assumed that the electrolytic friction, or the friction offered by other dissolved particles or by the molecules of the solvent itself, to the movement of the ions is, in dilute solutions, independent of the concentration. This assumption being borne in mind, the equation may be generalized to apply to monovalent or polyvalent ions as follows: —

$$\Lambda_D = x\,(u_o + u_e).$$

Here Λ_D represents the equivalent conductance of the electrolyte, or the conductance when one equivalent of it is dissolved in D cubic centimeters of the solvent, and x the per cent of the equivalent which is dissociated into ions, *i.e.* the degree of dissociation. By combining the equations —

$$\Lambda_\infty = u_o + u_e \text{ and } \Lambda_D = x\,(u_o + u_e),$$

where Λ_∞ represents the maximum value of the equivalent conductance or its value at infinite dilution, the value of x, or the degree of dissociation, can be calculated.

$$x = \frac{\Lambda_D}{\Lambda_\infty}.$$

The degree of dissociation of a substance in solution is equal to the ratio of its equivalent conductance in that solution to its equivalent conductance in a solution of infinite volume.

As has already been seen (see page 58), Arrhenius had come to this conclusion and had also found that the values of the degree of dissociation obtained from measurements of the freezing-point lowering of solutions agree satisfactorily with those calculated from the electrical conductance. The extent of this agreement is well shown in the carefully prepared article of A. A. Noyes.[1] According to this article, the values obtained by the two methods do not differ by more than two or three per cent between the concentrations 0.005 and 0.25 normal in the case of the salts, — NaCl, KCl, Na_2SO_4, K_2SO_4, and $BaCl_2$. It should also be mentioned in this connection that the experimentally determined values of the electromotive force of concentration cells (see the chapter on electromotive force) do not differ more than about one per cent from the values calculated with the aid of the dissociation values obtained from conductivity measurements.

The determination of the degree of dissociation of different substances has become a very important work.

Ostwald found that the order in which acids accelerate or catalyze

[1] *Technology Quarterly*, 17, No. 4, December, 1904.

the saponification of methyl acetate, or invert cane sugar, is also the order in which they compete for a base. The latter can be determined by either thermochemical or volume-chemical measurements. Thus a measure of the "strength" or "affinity" of an acid (or base) was obtained.

Arrhenius sought to discover the existence of a relation between electrical conductance and chemical activity, and found that, in reality, the two properties are closely related. As in the case of the equivalent conductance, the chemical activity or strength of an acid increases with the dilution and finally reaches a limiting value. Consider, for instance, two equivalent solutions of different acids. If the degree of dissociation is different in the two cases, then the chemical activities or strengths of the two acids will also be different. On diluting the two solutions the dissociation of each acid increases with a ratio of its own until, at great dilutions, it is complete. At such dilutions the two acids possess equal chemical activities or strengths. The *relative strengths* of acids and bases change, therefore, with the concentration. This was shown by Ostwald before the rise of the theory of electrolytic dissociation.

Application of the Mass-action Law to Gaseous and to Electrolytic Dissociation. — Accepting the dissociation theory, and the applicability of the gas laws to dissolved substances, as established by van't Hoff, *a dissociation or affinity constant*, which is independent of the dilution, may be calculated. This was first shown by Ostwald.[1]

According to the law of mass action, at constant temperature the following principle holds for a gas which dissociates into two components: —

The product of the active masses of the two components, divided by the active mass of the undissociated part, is a constant.

By the active mass of a substance is meant the number of mols of it which are contained in the unit volume. It is, therefore, identical with the molar concentration. In the case of gases, partial pressures, which are proportional to the active masses, may be substituted for the active mass in the above statement. Consider, for example, the dissociation of ammonium chloride, at a high and constant temperature, into hydrochloric acid and ammonia according to the equation: —

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$

Then according to the law of mass action,

$$\frac{p'_{NH_3} \times p'_{HCl}}{p_{NH_4Cl}} = \frac{p'^2}{p_{NH_4Cl}} = K_p$$

[1] *Ztschr. phys. Chem.*, 2, 270 (1888).

where p'_{NH_3}, p'_{HCl}, and p_{NH_4Cl} represent the partial pressures of ammonia, hydrochloric acid, and undissociated ammonium chloride, respectively, and K_d a constant characteristic of the equilibrium existing between these substances at the temperature in question but independent of the values of the single partial pressures. Thus, at the constant temperature, the gaseous mixture may be compressed or expanded, or an excess of any one of the constituents may be added, without changing the value of the constant or the form of the above equation. It is therefore evident that, whenever these three gases are brought together in whatever proportions at this constant temperature, such a rearrangement takes place in their individual concentrations, or partial pressures, that the above equation is still satisfied with the same value of the constant. Thus if ammonia gas be added to a given volume of the dissociated ammonium chloride, the partial pressure of the ammonia in the mixture is thereby increased. In this case, if the partial pressures of the hydrochloric acid and of the undissociated ammonium chloride did not undergo a change, the constant K_d would necessarily increase. Since, however, the constant K_d does not increase, either the numerator of the fraction

$$\frac{p'_{NH_3} \times p'_{HCl}}{p_{NH_4Cl}}$$

must decrease in value, the denominator increase, or both changes must take place simultaneously. The latter happens. A part of the ammonia combines with an equivalent quantity of hydrochloric acid to form undissociated ammonium chloride. This reaction progresses until again the mass action equation is satisfied. In this case, when equilibrium is again established, the values of p'_{NH_3} and p'_{HCl} are, of course, no longer equal.

Since, according to the theory established by van't Hoff, the behavior of solutes in dilute solutions is analogous to that of gases under small pressures, it may naturally be assumed that relations entirely similar to those applying in the case of the dissociation of ammonium chloride also hold for electrolytes which dissociate into two ions. For example, acetic acid in dilute aqueous solutions dissociates according to the equation,

$$CH_3COOH \rightleftarrows CH_3COO' + H'$$

Hence, according to the mass-action law, it would be expected that, at constant temperature, the following equation would hold: —

$$\frac{C_H \times C_{Ac}}{C_{HAc}} = \frac{C^2}{C_{HAc}} = K_d.$$

In this equation C_H, C_{Ac}, and C_{HAc} represent the active or molar masses of hydrogen ions, acetate ions, and undissociated acetic acid, respectively, and K_d a constant, called the *dissociation constant*, which is characteristic of the equilibrium between these three substances and independent of the individual concentration of each substance and of other substances which may also be present in the solution. The dissociation constant is characteristic of the compound and its determination is therefore of great importance.

In order to show the existence of this relation between the dissociated and undissociated parts of an electrolyte in dilute solution, it is, of course, necessary to have a method of finding, accurately, the concentrations of the ions and of the undissociated molecules. For this purpose the determination of the electrical conductance is most satisfactory, and it is in consequence of this fact that conductivity measurements are of such great value.

This method of testing the applicability of the law of mass action to electrolytes in dilute aqueous solution will now be considered. A mol of a binary electrolyte is dissolved in D cubic centimeters of water, in which it dissociates according to the equation,

$$A \rightleftarrows A' + B'.$$

The mass-action equation for this case is, then, —

$$\frac{C_{A'} \times C_{B'}}{C_{AB}} = K_d.$$

If x = the degree of dissociation of the electrolyte or that fraction of the mol which is broken up into the ions A' and B',

and $1-x$ = the fraction of the mol remaining in the undissociated state AB,

then $\frac{x}{D}$ = concentration, or active mass, of each of the ions A' and B',

and $\frac{1-x}{D}$ = concentration, or active mass, of the undissociated part, AB.

By substitution of these values in the above mass-action equation, the following is obtained: —

$$\frac{\frac{x}{D} \times \frac{x}{D}}{\frac{1-x}{D}} = K_d.$$

or
$$\frac{x^2}{(1-x)\,D} = K_d$$

It is evident that, in order to determine the dissociation constant, it is only necessary to know the dilution D and the degree of dissociation x of the solute. The former being already known, the latter is determined from measurements of the equivalent conductance of the solution at the two dilutions, D and infinity. As has already been stated, the dissociation is equal to the ratio of the former to the latter conductance, or, otherwise expressed,

$$x = \frac{\Lambda_D}{\Lambda_\infty}.$$

This value of x may be substituted in the equation,

$$\frac{x^2}{(1-x)\,D} = K_d,$$

with the following results: —

$$\frac{\left(\frac{\Lambda_D}{\Lambda_\infty}\right)^2}{\left(1-\frac{\Lambda_D}{\Lambda_\infty}\right)D} = K_d,$$

or
$$\frac{(\Lambda_D)^2}{\Lambda_\infty\,(\Lambda_\infty - \Lambda_D)\,D} = K_d.$$

Before proceeding further to the proof of this formula, it is advisable to become acquainted with the methods used for the determination of the conductance of solutions.

Determination of the Electrical Conductance of Electrolytes. The Method of Kohlrausch. — By an application of Ohm's law,

$$C = \frac{F}{R},$$

the resistance of metallic conductors, or conductors of the first class, may be measured in a very simple manner; but this is not the case with solutions of electrolytes, or conductors of the second class. The gradual fall of potential F which exists in that portion of the circuit occupied by a solution is, in most cases, scarcely to be determined accurately, because potential-differences which exist at the electrodes and the solution are made variable by the nature of the chemical decomposition or "polarization" taking place there. Many methods, of more or less value, have been devised for overcoming this diffi-

culty.[1] Of these methods only that one will be described in detail which is used almost exclusively at the present time for the determination of the electrical conductance of electrolytes, namely, the Kohlrausch method.

This method depends upon the use of an alternating current of high frequency, and of non-corrodible electrodes, which are platinized in order to increase their surfaces. By this method the disturbing influence of the chemical changes at the electrodes, or the "polarization," is practically removed; for the polarization effect produced by the current when flowing in one direction for a very small fraction of a second is practically neutralized by the effect produced when the current is reversed for the same small interval of time. The disturbing influence being thus removed, the resistance of the solution may be determined exactly as in the case of the conductors of the first class.

[The apparatus employed is essentially a Wheatstone bridge. Therefore, the principle of a Wheatstone bridge will be discussed before considering the form actually used in the determination of the conductance of solutions. A simple form of such a bridge is shown in Figure 28, in which the different parts are named. The direct

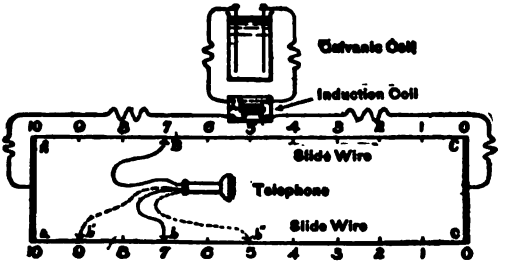


FIG. 28

current from the galvanic cell actuates the induction coil, thus causing an alternating current of high frequency to flow through the divided circuit consisting of the two branches AC and ac, respectively, which are uniform wires of different resistances extending between the metal bars Aa and Cc.

Let us now consider the relation between the fall in potential, the resistance, and the flow of the electric current in the different parts of the circuit during the momentary passage of electricity from Aa to Cc, assuming the potential at Aa to be ten units and at Cc zero. Then along each of the two wires AC and ac there is a

[1] Ostwald, *Lehrbuch der Allg. Chemie*, Vol. II, 1, 622.

fall of potential of ten units. This would also be true of any other wire, whatever its resistance, extending between the bars *Aa* and *Cc*. Since the two wires, although of widely different resistances, are each of uniform cross section, the fall of potential along them will be uniform. Thus along each tenth part of the distance between *Aa* and *Cc* on each wire there will be a fall in potential of one unit, as shown by the numerical values in the figure. These values, then, represent the potentials of the different points along the wires.

If now the point *B*, on the wire *AC*, at which the potential is seven units, be connected with the point *b*, on the wire *ac*, at which the potential is also seven units, it is clear that no electric current will flow through the connecting wire *Bb*, since there is no potential-difference between the ends of the wire. If, however, the point *B* is connected with the point *b'*, at which the potential is nine units, instead of with *b*, a current will flow through the wire from *b'* to *B*, since a potential-difference exists between the ends of the wire. Finally, if the point *B* is connected with the point *b''*, at which the potential is five units, instead of with *b'*, there will again be a difference of potential of two units between the ends of the connecting wire, and, therefore, an electric current will flow through it. In this case the direction of the current is the reverse of that in the previous case. It may then be stated that whenever a connecting wire extends between equipotential points of the branches of a divided circuit no current flows through it. In all other cases a current does flow through the wire. As a means of detecting whether or not an alternating current is flowing in the connecting wire a telephone receiver is introduced into its circuit as shown in the figure. When a current flows (as for instance when *B* and *b'* are connected) a humming sound is heard in the telephone. If now the end of the wire at *b'* is moved along the wire to *b* and then to *b''*, the humming sound diminishes, going through a sharp minimum when the point *b* is reached, and rising again as the point *b''* is approached. By listening at the telephone it is then possible to tell when the wire connects equipotential points.

It is at once evident from the figure that when the wire connects equipotential points, as, for example, *B* and *b*, the following relation exists between the fall in potential in the different parts of the two branches of the divided circuit, otherwise known as the arms of the Wheatstone bridge: —

Fall in *AB* : Fall in *BC* = Fall in *ab* : Fall in *bc*.

Recalling to mind the fact that the falls in potential in the different parts of a circuit are directly proportional to the respective resistances of the parts, in this case it follows that

Resistance AB : Resistance BC = Resistance ab : Resistance bc.

If now the ratio of any two of these resistances, such as, for example, the ratio of the resistance of ab to that of bc, and the actual value of either of the two resistances, AB or BC, are known, then the fourth, or the unknown resistance, may be calculated from the above proportion.

In this manner unknown resistances may be determined by means of the Wheatstone bridge.

When the resistance of an electrolyte is to be determined the Wheatstone bridge is arranged as shown in Figure 29.[1] The

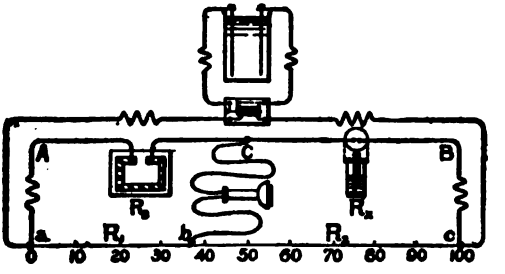


FIG. 29

similarity between this figure and the one directly preceding it is at once evident. In this figure the two branches of the divided circuit are abc and $aABc$, respectively. The former branch includes a resistance box, by means of which various known resistances can be introduced into the circuit, and the conductivity cell containing the solution to be investigated. The resistances in the resistance box and in the conductivity cell are so great that those of the connecting wires in this branch may be neglected. The branch abc consists of a platinum wire of uniform resistance, which is either stretched over a meter scale or wound on a drum, which is marked off in millimeter lengths. One end of the connecting wire Cb is made fast at any point C between the resistance box and the conductivity cell, while the other end b is connected with the platinum wire by means of a sliding contact. The position of this sliding contact may be read off on the meter or drum scale to tenths of a millimeter. In series

[1] Ostwald, *Ztschr. phys. Chem.*, **2**, 561 (1888).

with the connecting wire is a telephone receiver (naturally a galvanometer cannot be used), which serves to determine when the sliding contact is in such a position that no current flows through the wire, *i.e.* when the wire connects equipotential points. The four arms of the Wheatstone bridge are then *ab*, *bc*, *aAC*, and *CBc*. Hence when the sliding contact is in the position giving a minimum tone in the telephone receiver, the following relations obtain: —

$$\frac{\text{Resistance of } ab}{\text{Resistance of } bc} = \frac{\text{Resistance in box}}{\text{Resistance in cell}}.$$

If the platinum wire is of uniform resistance, we have —

$$\frac{\text{Resistance of } ab}{\text{Resistance of } bc} = \frac{\text{Distance } ab}{\text{Distance } bc}$$

Therefore,

$$\text{Resistance in cell} = \text{Resistance in box} \times \frac{\text{Distance } bc}{\text{Distance } ab},$$

or,

$$R_x = R_2 \times \frac{bc}{ab}.$$

The absolute value of the resistance of the platinum wire evidently does not come into consideration, since only the *ratio* of the resistances of the two parts of it is required.]

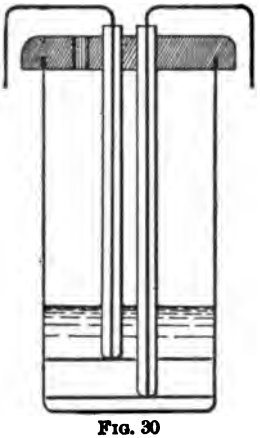


FIG. 30

A vessel, such as is shown in Figure 30,[1] can in most cases be used for the determination of the conductance of an electrolyte.

The area of the electrodes and the distance between them can be varied as desired. In general, it is advantageous to platinize them, using a solution containing about three per cent of commercial platinic chloride and about 0.025 per cent of lead acetate.

If the distance in centimeters between the two electrodes is represented by l, and their area in square centimeters by s, then the value of the specific conductance K is given by the following equations: —

$$K = \frac{1}{R_x} = \frac{ab}{R_2 \times bc} = K\frac{s}{l}.$$

Hence

$$K = \frac{l}{R_x s}.$$

[1] For other forms of conductivity cells, see Ostwald-Luther's *Physik.-chem. Messungen*, page 401.

From the specific conductance κ, and the equivalent dilution of the solution D in cubic centimeters, the value of the equivalent conductance can be calculated in the manner described on page 86, with the aid of the equation,

$$\Lambda = \kappa \times D,$$

providing the cross section of the vessel and the areas of the electrodes are practically the same. In order to avoid this proviso and to obviate the necessity of measuring the space between the electrodes, it is usual to determine the so-called "*cell constant*" of the conductance cell. The cell constant is equal to the resistance found in the cell when it contains between the electrodes a solution of a specific conductance, or conductivity, of unity. In this cell, since the conductivity of the solution is unity,

$$R_x = \frac{l}{s} \times k = K_c,$$

where R_x is the measured resistance, k a constant depending upon the form of the cell and the position of the electrodes in reference to the cell walls, and K_c the cell constant. When the surfaces of the electrodes are equal to the cross section of the cell, the value of k becomes unity.

It is not at all necessary, however, to have a solution whose specific conductance is unity in order to obtain the value of the cell constant. It can be obtained with the aid of any liquid of known conductance. Thus, if the specific conductance of the liquid is κ, and its resistance when in the cell whose constant is to be determined is R, then the value of the cell constant K_c is given by the equation,

$$K_c = R \times \kappa.$$

When the cell constant is known, the specific and equivalent conductances of any liquid may be obtained with the use of the equations,

$$\kappa = \frac{K_c}{R_x} \text{ or } \Lambda = D\,\frac{K_c}{R_x},$$

where R_x is the resistance of the liquid as measured directly on the Wheatstone bridge. If the conductance of the liquid used to obtain the cell constant is expressed in ohms, then the specific or the equivalent conductance, calculated according to the above equations, is also expressed in ohms, even though the resistance in the resistance box used both to obtain the cell constant and to obtain the unknown conductance is expressed in other units.

In determining the cell constant, a 0.02 normal solution of potassium chloride is often used as the liquid of known conductance. According to the most recent measurements, its specific conductance, or conductivity, at 18° and at 25° is

$$K_{18^\circ} = 0.002399, \text{ and } K_{25^\circ} = 0.002773,$$

while its corresponding equivalent conductance is

$$K_{18^\circ} = 119.96, \text{ and } K_{25^\circ} = 138.67.$$

The value of the equivalent conductance is a large one. The resistance of one equivalent of potassium chloride in this solution, when placed between electrodes one centimeter apart, is accordingly $\frac{1}{119.9}$ and $\frac{1}{138.7}$ ohms, respectively.

The equivalent conductances of all binary electrolytes, at infinite dilution, are of the same order of magnitude, varying between 50 and 500, as may be seen from the table on page 93. On the other hand, the value of the equivalent conductance, at other dilutions, may be exceedingly small for some electrolytes. This will be evident from a glance at the table on page 88.

Method of Nernst and Haagn.[1]—This method of determining conductance permits an easy measurement of the internal resistance of a cell even while a current is passing through it. It is characterized by the use of two condensers, in place of two of the resistances employed in the Wheatstone bridge. The arrangement of the apparatus is shown in Figure 31.

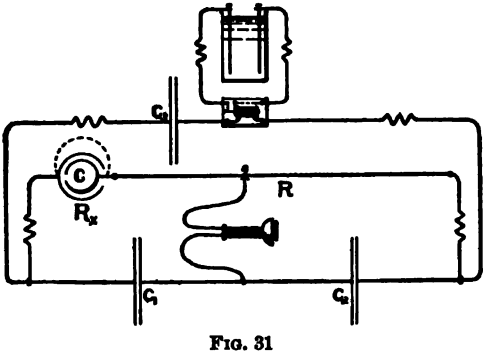


FIG. 31

The condenser C_2 is used to prevent closing the circuit of the cell C, the internal resistance of which is to be measured. Under these

[1] *Ztschr. Elektrochem.*, **2**, 493 (1896); *Ztschr. phys. Chem.*, **23**, 97 (1897).

circumstances the cell produces no current. After the known resistance R has been varied until a minimum tone is heard in the telephone receiver, the value of the unknown resistance R_x of the cell C may be calculated from the equation,

$$R_x : R = C_2 : C_1,$$

where C_2 and C_1 represent the respective capacities of the two lower condensers. The ratio $C_2 : C_1$ must be determined independently. This can be done by means of an ordinary Wheatstone bridge.

In order to obtain the internal resistance of a cell while producing an electric current, the cell is short-circuited through a known resistance as indicated in the figure by the dotted line. It must be clearly understood that the real internal resistance R_x of the cell is not obtained by direct measurement, but is obtained from the measured resistance R_x' and from the resistance of the dotted shunt circuit, according to the equation:—

$$\frac{1}{R_x'} = \frac{1}{R_x} + \frac{1}{R_x''}.$$

The value of R_x'' may be obtained with sufficient exactness from the equation,

$$R_x = R_x' \left(1 + \frac{R_x'}{R_x''}\right).$$

Calculation of the Dissociation Constant from Electrical Conductance. — It has already been shown that the dissociation constant may be calculated by the aid of the equation,

$$K_d = \frac{K_D^2}{K_\infty (K_\infty - K_D) D}.$$

In order to obtain the value of the constant, it is therefore necessary to know both the value of the equivalent conductance at dilution D, or K_D, and that at dilution infinity, or K_∞. The method of obtaining the value of K_D has already been considered. In some cases the value of K_∞ may be obtained by the same method, it being placed equal to the maximum value of the equivalent conductance found upon diluting the solution. This method is applicable only to electrolytes which dissociate to a large degree in solutions of ordinary dilutions. It is not applicable to other electrolytes, because, at the extreme dilutions at which the value of K could be considered equal to K_∞, it is impossible to determine the conductance of the solution. This is the case with practically all organic acids and bases, where a knowledge of the value of the dissociation constant is

of special importance. Fortunately, however, the alkali salts of all acids and the halogen salts of practically all bases are largely dissociated in moderately dilute solutions, and nearly completely dissociated in solutions the conductance of which can still be determined. Thus the value of K_∞ for these salt solutions may be determined by direct experiment. But this value has been shown to be equal to the sum of the migration velocities of anion and cation:—

$$K_\infty = v_c + v_a.$$

[In the case of the alkali salt of a slightly dissociated acid HA, K_∞ may be determined directly, and v_c is a known value. The value of v_a for the anion A′ is thereby determined. But the value of v_c for the cation H˙, is a known value. Hence the value of K_∞ for the acid HA may at once be obtained by adding together the known migration velocities of its ions. Thus

$$K_\infty \text{ (for HA)} = v_c \text{ (for H˙)} + v_a \text{ (for A′)}.$$

In a similar manner the equivalent conductance at infinite dilution for a slightly dissociated base, BOH, may be obtained. For its halogen salt, K_∞ can be determined directly, and v_a for the halogen ion is known. Hence the value of v_c for the cation B˙ is known. From this value and the known value of v_a for the anion OH′ the equivalent conductance of the base BOH at infinite dilution may be obtained by the aid of the equation,

$$K_\infty \text{ (for BOH)} = v_c \text{ (for B˙)} + v_a \text{ (for OH′)}.$$

In the above explanation of the indirect method of determining the value of the equivalent conductance of a slightly dissociated acid or base at infinite dilution, the individual migration velocities of the ions were involved. This is not at all necessary in making actual calculations, as will be made evident from a reconsideration of the above acid HA. The value of K_∞, for example, of hydrochloric acid, of sodium chloride, and of the sodium salt of the acid HA may be obtained from direct measurements on very dilute solutions. Hence the three equations,

$$\begin{aligned} K_\infty \text{ (for HCl)} &= v_c \text{ (for H˙)} + v_a \text{ (for Cl′)}; \\ K_\infty \text{ (for NaCl)} &= v_c \text{ (for Na˙)} + v_a \text{ (for Cl′)}; \\ K_\infty \text{ (for NaA)} &= v_c \text{ (for Na˙)} + v_a \text{ (for A′)}. \end{aligned}$$

Combining these equations,

$$\begin{aligned} K_\infty \text{ (HCl)} - K_\infty \text{ (NaCl)} + K_\infty \text{ (NaA)} &= v_c \text{ (H˙)} + v_a \text{ (A′)}; \\ K_\infty \text{ (HCl)} - K_\infty \text{ (NaCl)} + K_\infty \text{ (NaA)} &= K_\infty \text{ (HA)}. \end{aligned}$$

The latter equation, in which migration velocities do not appear, may be used for the calculation of the value of Λ_∞ for the acid in question.] As is evident, it is only necessary to add to the difference of the values of Λ_∞ for hydrochloric acid and sodium chloride, the value of Λ_∞ for the sodium salts of any slightly dissociated acid, to obtain the equivalent conductance of the latter acid at infinite dilution. The values of Λ_∞ for hydrochloric acid and sodium chloride according to most recent measurements, and their differences, are given in the following table:—

Temperature	Λ_∞ for HCl	Λ_∞ for NaCl	Difference
18°	383.4	108.9	274.5
25°	427.1	126.6	300.5

From the values of the equivalent conductance at the dilution D and at the dilution infinity, obtained as above described, the dissociation constants have been calculated for a large number of slightly dissociated acids and bases at different dilutions. It was found that the constants are independent of the concentration. The results obtained for acetic acid are given in the following table:—

Equivalent Concentration	Dissociation Constant × 10^5.
$\frac{1}{8}$	0.00180
$\frac{1}{16}$	0.00179
$\frac{1}{32}$	0.00182
$\frac{1}{64}$	0.00179
$\frac{1}{128}$	0.90179
$\frac{1}{256}$	0.00180
$\frac{1}{512}$	0.00180
$\frac{1}{1024}$	0.00177

The value of the dissociation constant may serve in many cases as a trustworthy aid in the identification of a compound.[1]

Since a consideration of the significance of this constant belongs to the subject of chemical statics, it will not be discussed further here. It may be well to state, however, that the order of magnitudes of these constants for different compounds is also the order of their degrees of dissociation in solutions of the same equivalent concentration. A direct proportionality does not exist between the constants and the degrees of dissociation, for, as the dilution is increased, the latter approaches a constant value. Nevertheless, some

[1] Scudder, *J. Phy. Chem.*, 7, 269 (1903).

conclusions from the existence of such constants, which were empirically established by Ostwald before the dissociation theory was proposed, will be considered.

1. With increasing value of D in the equation,

$$\frac{(\mathbb{K}_D)^2}{\mathbb{K}_\infty (\mathbb{K}_\infty - \mathbb{K}_D)} = K_d \times D,$$

the left-hand side finally becomes infinite. Since $\mathbb{K}_D$ and $\mathbb{K}_\infty$ are always finite quantities, this can only be true when

$$\mathbb{K}_D = \mathbb{K}_\infty.$$

The equivalent conductance approaches its value at infinite dilution as the dilution is increased.

2. In the case of slightly dissociated, and consequently poorly conducting, binary electrolytes, where $\mathbb{K}_D$ is very small in comparison with $\mathbb{K}_\infty$, the expression $(\mathbb{K}_\infty - \mathbb{K}_D)$ changes but slightly with the dilution and may therefore be considered as a constant. Hence the equation,

$$\frac{\mathbb{K}_D^2}{D} = \text{Constant.}$$

The equivalent conductance increases with increasing dilution in proportion to the square root of the dilution; or the square of the equivalent conductance increases in proportion to the dilution.

3. If the mass-action equation for the dissociation be written in its original form as follows:—

$$\frac{x^2}{(1-x)D} = K_d,$$

then for substances which dissociate but slightly, the value of $1-x$ may be considered as unity without serious error and the equation assumes the form,

$$\frac{x^2}{D} = K_d.$$

In the case of slightly dissociated electrolytes, the dissociation constant varies directly as the square of the percentage dissociation and inversely as the dilution.

4. According to the derivation given in No. 2, the following equations hold for two or more slightly dissociated electrolytes:—

$$\frac{(\mathbb{K}'_{D'})^2}{D'} = \text{Constant,}$$

and

$$\frac{(\mathbb{K}''_{D''})^2}{D''} = \text{Constant, etc.}$$

These two equations may be combined, resulting in the equation,

$$\frac{\frac{(\mathbb{K}'_D)^2}{D'}}{\frac{(\mathbb{K}''_D)^2}{D''}} = \text{Constant.}$$

If now the dilution of one of the electrolytes (D') is equal to that of the other (D''), then the equation becomes

$$\frac{(\mathbb{K}'_D)^2}{(\mathbb{K}''_D)^2} = \text{Constant.} \qquad (a)$$

From the equations derived in No. 3, it may be shown in a similar manner that the following equation holds: —

$$\frac{(x')^2}{(x'')^2} = \frac{K'_d}{K''_d}. \qquad (b)$$

In the above equations, $\mathbb{K}'_D$, x', K'_d, and $\mathbb{K}''_D$, x'', and K''_d represent the equivalent conductances at dilution D, the degrees of dissociation, and the dissociation constants of the two electrolytes respectively. It has been shown that

$$\mathbb{K}_D = \mathbb{K}_\infty x.$$

Hence for the above electrolytes we have the equation,

$$\frac{\mathbb{K}'_D}{\mathbb{K}''_D} = \frac{\mathbb{K}'_\infty x_1}{\mathbb{K}''_\infty x_2}.$$

If now the value of $\mathbb{K}'_\infty$ is equal to that of $\mathbb{K}''_\infty$, such as is the case with many acids because of the very great migration velocity of the ion which they have in common (the hydrogen ion), this equation becomes

$$\frac{\mathbb{K}'_D}{\mathbb{K}''_D} = \frac{x'}{x''}. \qquad (c)$$

Combining equations (b) and (c), the following equation results: —

$$\frac{(\mathbb{K}'_D)^2}{(\mathbb{K}''_D)^2} = \frac{K'_d}{K''_d}.$$

The squares of the equivalent conductances of different electrolytes at the same dilution are to each other as the corresponding dissociation constants.

5. In the equation —

$$\frac{(\mathbb{K}_D)^2}{\mathbb{K}_\infty(\mathbb{K}_\infty - \mathbb{K}_D)D} = K_d,$$

the value of $\mathbb{K}_D$ may, in the case of electrolytes which dissociate to a large degree, be considered as remaining practically constant with increasing dilution, and as $\mathbb{K}_\infty$ is in itself constant, the equation becomes

$$\frac{1}{(\mathbb{K}_\infty - \mathbb{K}_D)D} = \text{Constant.}$$

The difference between the equivalent conductance at a given dilution and that at the dilution infinity multiplied by the former dilution gives a constant value.

6. In the case of electrolytes which dissociate to a large extent, the value of the percentage dissociation x may be considered as approximately equal to unity. The equation

$$\frac{x^2}{(1-x)D} = K_d$$

may then be written in the simple form,

$$\frac{1}{(1-x)D} = K_d, \text{ or } (1-x)D = \frac{1}{K_d}.$$

The undissociated portion of an electrolyte multiplied by the dilution is equal to the reciprocal of the dissociation constant.

According to this statement, it is evident that if the undissociated portion at an equivalent dilution of 50,000 cubic centimeters amounts to one per cent, it will amount to only one half per cent at a dilution of 100,000 cubic centimeters.

7. According to the derivation of No. 5, the following equations hold for any two electrolytes which are largely dissociated: —

$$(\mathbb{K}'_\infty - \mathbb{K}'_{D'})D' = \text{Constant},$$

and

$$(\mathbb{K}''_\infty - \mathbb{K}''_{D''})D'' = \text{Constant}.$$

These equations combined give the following: —

$$\frac{(\mathbb{K}'_\infty - \mathbb{K}'_{D'})D'}{(\mathbb{K}''_\infty - \mathbb{K}''_{D''})D''} = \text{Constant}.$$

When the dilution of one electrolyte D' is equal to that of the other D'', this equation becomes —

$$\frac{\mathbb{K}'_\infty - \mathbb{K}'_{D'}}{\mathbb{K}''_\infty - \mathbb{K}''_{D''}} = \text{Constant}. \qquad (a)$$

In a similar manner, from the derivation of No. 6 the following equation may be obtained: —

$$\frac{1-x'}{1-x''}=\frac{K'}{K''}. \qquad (b)$$

The latter equation may be expressed in words as follows: —

The undissociated portions of different electrolytes at the same equivalent dilution are inversely proportional to their dissociation constants.

When the equivalent conductances of the two electrolytes at infinite dilution are nearly the same, equations (*a*) and (*b*) may be combined, giving the approximate equation,

$$\frac{\Lambda'_\infty-\Lambda'_D}{\Lambda''_\infty-\Lambda''_D}=\frac{K''_d}{K'_d}.$$

The differences between the equivalent conductance at a given dilution and that at infinite dilution of two electrolytes are inversely proportional to their dissociation constants.

8. Finally, the following regularities for all electrolytes may be deduced. If two electrolytes are dissociated to the same extent, then the left side of the equation,

$$\frac{x^2}{1-x}=K_d\cdot D,$$

is the same for both, and, consequently, the same is true of the right side.

Hence the equation,

$$D'\times K'_d=D''\times K''_d$$

or

$$\frac{D'}{D''}=\frac{K''_d}{K'_d}.$$

The equivalent dilutions at which different electrolytes possess the same degree of dissociation (and also often nearly the same equivalent conductance) are in a constant ratio to each other, which is equal to the inverse ratio of the respective dissociation constants.

The foregoing approximations may often be used with advantage.

Relation between Dissociation Constants and Chemical Constitution. Some very interesting relations have been found between the magnitudes of the dissociation constants and the chemical constitution of acids, as may be illustrated by a few examples. The constants ($K_d\cdot 10^5$) for acetic acid and the three chloracetic acids, at 25°, are as follows: —

Acetic acid	(CH_3COOH)	0.00180
Monochloracetic acid . .	($CH_2ClCOOH$)	0.155
Dichloracetic acid . . .	($CHCl_2COOH$)	5.14
Trichloracetic acid . .	(CCl_3COOH)	121.

Thus the replacement of the hydrogen by chlorine causes a very large increase in the value of the constant. That this increase is not the same for the successive replacements by chlorine is evident from the following table: —

Replacement	Increase in Constant
First	$\frac{0.155}{0.00180}$, or 86 fold.
Second	$\frac{5.14}{0.155}$, or 33.2 fold.
Third	$\frac{121}{5.14}$, or 23.5 fold.

It may be concluded from this that the introduction of chlorine into acetic acid produces an effect somewhat different from that which it produces when introduced into chloracetic acid. This is not surprising, since a chlorine atom is already present in the latter compound. An increase in the value of the dissociation constant indicates an increase in the degree of dissociation, and also an increase in the intensity of its acid character. The replacement of hydrogen by chlorine produces an effect in this direction. The introduction of such other so-called negative radicals as Br, CN, SCN, OH, etc., also increases the acid character of the original compound in a similar manner.

The α and β substituted derivatives of acids possess very different dissociation constants, thus showing the marked constitution property of this constant. The same applies to the isomeric derivatives of benzene, for example: —

Benzoic acid	C_6H_5COOH	0.006
o-Hydroxybenzoic acid . .	*o*-$C_6H_4(OH)COOH$ . . .	0.102
m-Hydroxybenzoic acid . .	*m*-$C_6H_4(OH)COOH$ . . .	0.0087
p-Hydroxybenzoic acid . .	*p*-$C_6H_4(OH)COOH$ . . .	0.00286

These examples show that a knowledge of the dissociation constant is of aid in the determination of the chemical constitution of compounds. By the introduction of an hydroxyl group into benzoic acid in the ortho position, the constant for the acid is increased seventeen fold. When the same group is, instead, substituted in the meta position, the change from the benzoic acid value is slight, but still positive, while an entrance into the para position even causes a considerable reduction of the constant. Consequently, it might be assumed that if a series of acids be formed by introducing

hydroxyl groups into ortho-oxybenzoic acid, their dissociation constants would vary in a similar manner. That this is the case is evident from a consideration of the following table: —

o-Oxybenzoic (salicylic) acid	$C_6H_4(OH)COOH$	0.102
Hydroxysalicylic acid . .	$C_6H_3(OH)_2COOH$ (2, 3) . . .	0.114
Hydroxysalicylic acid . .	$C_6H_3(OH)_2COOH$ (2, 5) . . .	0.108
Resorcylic acid	$C_6H_3(OH)_2COOH$ (2, 4) . . .	0.052
Resorcylic acid	$C_6H_3(OH)_2COOH$ (2, 6) . . .	5.0

In the acid (2, 3) and also in the acid (2, 5) the new hydroxyl group is in the meta position in relation to the carboxyl group. Consequently, only a very slight increase in the dissociation constant is to be expected. This agrees with experimental observation.

In the acid (2, 4) the new hydroxyl group occupies the para position, and, as in the case of hydroxybenzoic acids, a new constant, less than the original one, results. Finally, when the second hydroxyl group occupies the remaining ortho position, as in the acid (2, 6), a corresponding great increase in the constant is found, the increase being about fifty fold.

Interesting relations have been found in the case of the dissociation in stages of dibasic organic acids. From the fact that the mass-action equation for the dissociation of binary electrolytes holds also for weak dibasic acids, it follow that the dissociation takes place at first according to the equation,

$$H_2R \rightleftarrows H^{\cdot} + HR'. \qquad (a)$$

Only in the case of strong acids does a further dissociation according to the equation

$$HR' \rightleftarrows H^{\cdot} + R'' \qquad (b)$$

take place. In such cases the equation

$$\frac{x^2}{(1-x)\,D} = K_v$$

derived for binary electrolytes, naturally does not apply. Different dibasic or polybasic acids are strikingly characterized by the way in which they dissociate. While in the case of some acids the dissociation of the second hydrogen, according to equation (*b*), takes place only after that of the first hydrogen, according to equation (*a*), is nearly complete, in the case of other acids the dissociation

of the second hydrogen takes place to some extent when but fifty per cent of the first hydrogen is dissociated. This difference is evident in the titration of acids with indicators. Sulfurous acid, for example, when titrated, using litmus as an indicator, gives no sharp end point, the dissociation of the second hydrogen being too slight. However, succinic acid, which in respect to the first hydrogen ion is far less dissociated than sulfurous acid, may be easily titrated with the use of this indicator.

Between the dissociation constant for the dissociation of the first hydrogen atom (dissociation constant of the free acid) and the corresponding constant for that of the second hydrogen atom there exists the following relation: —

1. *The first hydrogen atom is dissociated to the greater, and the second to the lesser extent, the nearer the two carboxyl groups are to each other. The reverse is also true.*

This statement was first made by Smith,[1] who based it upon his own work and also that of Ostwald and Noyes.

As an illustration of this principle, the following quotation from Ostwald is given, in which it is assumed that the electrical charge of the acid ion is localized on the hydroxyl oxygen of the carboxyl group: —

"In the case of the dissociation of the first hydrogen atom of dibasic organic acids, the one carboxyl group exerts a negative influence upon, and tends to increase the degree of the dissociation of, the other carboxyl group. This tendency is the stronger, the nearer the two carboxyl groups are to each other. If the first stage of the dissociation takes place according to the equation

$$H_2R \rightleftarrows H^{\cdot} + HR'$$

then the second stage, $HR'H^{\cdot} \rightleftarrows + R''$

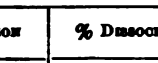
will in general take place far more difficultly than the first stage, since the negatively charged ion HR′ in dissociating must take up an extra negative charge to form the ion R″, and since the two negative charges repel one another. Secondly, the ease with which the second stage of the dissociation will take place depends upon the distance between the charges. Thus the nearer the charges on a bivalent ion are to each other, the less is the tendency of the hydrogen atom to split off, and conversely."

The behavior of fumaric and maleic acids is in complete agree-

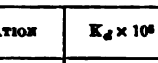
[1] *Ztschr. phys. Chem.*, **25**, 144 (1898).

ment with the above principle and hypothesis. This will be evident from a study of the following formulæ and tables:—

Maleic Acid



Fumaric Acid



Mol. Dilution	% Dissociation	$K_d \times 10^6$	% Dissociation	$K_d \times 10^6$
128	68.8	1.16	29.3	0.095
256	78.8	1.14	39.0	0.097
512	87.1	1.15	50.3	0.099
1024	92.8	1.17	63.9	0.110
2048	98.2	—	78.5	0.140

The per cent dissociation is calculated on the assumption that the acids dissociate as if they were monobasic.

The carboxyl groups in the fumaric acid molecule are farther apart than those in the maleic acid molecule. Corresponding to this, the dissociation constant is much less in the former than in the latter case. On the other hand, the dissociation of the second hydrogen takes place appreciably in the case of maleic acid only after a nearly complete dissociation of the first hydrogen atom, while in the case of fumaric acid it takes place when but about fifty per cent of the first hydrogen atom is ionized. This is indicated in the above tables by the increase in the value of the constant. The acid salts show an analogous behavior in respect to the dissociation of the second hydrogen atom. At a molar dilution of 64, the dissociation of this atom is 0.39 per cent in the case of the acid salt of maleic, and 0.85 per cent in that of fumaric, acid.

The effect of substituted groups in organic dibasic acids upon the dissociation of the second hydrogen atom is expressed in the following statement:—

2 *a*. *The degree of dissociation of the second hydrogen atom of all substituted acids is less than that of the original acid, except in the case of hydroxyl substituted acids, in which it is increased.*

Thus the dissociation of the second hydrogen atoms of methyl- and ethyl-succinic acids is less, and of the hydroxysuccinic acids, malic and tartaric acids, is greater, than that of succinic acid itself.

The relation between the dissociation constants of the first and second hydrogen acids of analogous substituted dibasic acids may be expressed as follows:—

2 *b*. *The dissociation constant* (K''_d) *of the second hydrogen atom*

of a substituted acid is the smaller, the greater the constant (K'_d) of the first hydrogen atom. In other words, the substituted groups affect the dissociation of the two hydrogen atoms oppositely.

While, for example, the value of K'_d for methyl- and ethyl-succinic acids is greater, the value of K''_d for these acids is less than the corresponding constant K_d for succinic acid.

A knowledge of the dissociation constant of the second hydrogen atom would undoubtedly, in many cases, be of an importance equal to that of the first hydrogen, in the study of the constitution of dissolved substances.[1]

Finally, it should be mentioned that with the aid of the dissociation constants of weak acids the degree of hydrolysis of their alkali salts may easily be calculated.[2]

Velocity of Migration of Individual Ions. — From conductance measurements not only have the dissociation constants of a large number of organic acids and bases been determined, but also the relative velocities of migration of the organic cations and anions. It has already been stated that the sodium and potassium salts of acids and the chlorides and nitrates of bases are dissociated to such a degree that the equivalent conductance at infinite dilution Λ_∞ is experimentally determinable. By subtraction of the known velocity of migration of the sodium, potassium, nitrate, or chlorine ion, as the case may be, from this value of Λ_∞, the velocity of the migration of the other ion of the compound is obtained (see page 106).

Through a stoichiometrical comparison of the numbers representing the migration velocities of the individual ions, certain relations have been discovered, some of which will be mentioned. These are taken from the comprehensive work of Bredig.[3]

The migration velocity of ions of elementary substances is a periodic function of the atomic weight. It increases with increasing atomic weight in any series of related elements. In these cases, the rule applies that considerable differences occur with the first two or three members of each series. Moreover, similar or related elements whose atomic weights are greater than thirty-five migrate with nearly the same velocity. These statements are illustrated by the following results obtained at 18° *t*. See also the values given on page 93.

[1] For further relationships between the chemical constitution and the affinity constants, see Wegscheider, *Wien. Monatshefte*, **23**, 287 (1902).

[2] Walker, *Ztschr. phys. Chem.*, **32**, 137 (1900).

[3] *Ztschr. phys. Chem.*, **13**, 191 (1894).

Element	Atomic Weight	u_∞	Element	Atomic Weight	u_∞
Lithium	7	33.4	Fluorine	19	46.6
Sodium	23	43.5	Chlorine	35	65.4
Potassium	39	64.7	Bromine	80	67.6
Rubidium	85	67.6	Iodine	127	66.4
Cæsium	133	68.2			

For complex ions the following principles have been established.

Isomeric ions migrate with the same velocity, as is evident from the following values:[1]—

Isomeric Anions	u_∞	Isomeric Cations	u_∞
Butyric	30.7	Propyl ammonium	40.1
Isobutyric	30.9	Isopropyl ammonium	40.0
Cinnamic	27.3	Chinolin methylium	36.5
Atropic	27.1	Isochinolin methylium	36.6

Similar changes in the composition of analogous ions produce changes in the same direction in the respective migration velocities. The magnitude of these changes does not remain constant for successive changes in the composition, but decreases with decreasing migration velocity. In other words, as the number of atoms are increased in an ion, or as an ion becomes more complicated in its structure, its migration velocity decreases, tending towards the general minimum value for univalent anions and cations, namely, about seventeen to twenty reciprocal Siemens units. A glance at the following values will make this more evident: —

Ion	Symbol	Velocity	Difference per CH_2
Ammonium	NH_4	70.4	
Dimethyl ammonium	$NH_2(CH_3)_2$	50.1	2(10.2)
Diethyl ammonium	$NH_2(C_2H_5)_2$	36.1	2(7.0)
Dipropyl ammonium	$NH_2(C_3H_7)_2$	30.4	2(2.9)
Dibutyl ammonium	$NH_2(C_4H_9)_2$	26.9	2(1.8)
Diamyl ammonium	$NH_2(C_5H_{11})_2$	24.2	2(1.4)

In analogous series of anions and cations of the same valence, the migration velocity is diminished:—

[1] These values have been taken directly from the article by Bredig, and are expressed in reciprocal Siemens units. Temperature = 25° t.

a. By the addition of hydrogen, carbon, nitrogen, chlorine, and bromine.

b. By the replacement of hydrogen by chlorine, bromine, iodine, etc.

In general, the more complicated the ion, the lower is its migration velocity. Accordingly, a polymeric ion moves more slowly than a simple one.

The effect of added atoms or atom-groups on the migration velocity of an ion is often obscured by the effect of the constitutional differences. Thus metameric ions, although of the same composition, migrate with different velocities because of their different constitutions. In general, in the case of such organic cations, the migration velocity increases with the degree of symmetry, as, for example, in passing from the primary form to the secondary, the secondary to the tertiary, etc. This is illustrated by the values for the cations of the series of bases given in the following table:—

Form	Ion	Symbol	Velocity
Primary	Xylidine	$C_8H_{12}N$	30.0
Secondary	Ethyl aniline	$C_8H_{12}N$	30.5
Tertiary	Dimethyl aniline	$C_8H_{12}N$	33.8
	Collidine	$C_8H_{12}N$	34.8
Quaternary	Pecoline ethylium	$C_8H_{12}N$	35.1
	Lutidine methylium	$C_8H_{12}N$	35.2

Thus the effect of added atoms or atom-groups on the additivity, particularly in the case of cations, is often destroyed by the opposing influences of such constitutional differences. Indeed, the direction of the additive change may even be reversed through over compensation by the constitutional changes, as in the following case:—

Ion	Symbol	Velocity
Triethyl ammonium	$(C_2H_5)_3 \equiv N-H$	32.6
Methyl-triethyl ammonium	$(C_2H_5)_3 \equiv N-CH_3$	34.4

In spite of the fact that the latter ion contains one CH_2 group more than does the former, no retardation, but, on the contrary, an acceleration, of the migration velocity takes place.

In the case of the migration velocity of polyvalent ions of organic acids, Wegscheider[1] has called attention to the following noteworthy regularities:—

The ratio of the migration velocities of bivalent and univalent ions containing the same number of atoms is approximately equal to a constant value (1.78). The same also holds true for the ratio of the migration velocities of bivalent and univalent ions when the latter contain one atom more than the former. In this case the same acid is formed from the bivalent and from the corresponding univalent ion and the value of the ratio is 1.81. The same relationship holds approximately for inorganic acids, as follows:—

Bivalent Ion	u_a	Univalent Ion	u'_a	$u_a + u'_a$
HPO_4''	55.0	H_2PO_4'	33.5	1.64
$HAsO_4''$	54.6	H_2AsO_4'	31.7	1.72

These relations are also of interest theoretically. It is a natural assumption that the resistance encountered by a moving ion is independent of the number of electrical charges carried by the ion. Furthermore, since the force driving the ion is, in the same electrical field, proportional to the electrical charges on the ion, it would be expected that the migration velocity of an ion would be doubled if to its first charge another be added. However, as has been seen, observation is not entirely in agreement with this conclusion. Hence we must conclude that the resistance opposing the movement of an ion is influenced by the extra charge upon the ion. To explain this, it may be conceived that the volume, and consequently the frictional resistance, of the ion is increased by the mutual repellent action of the two charges of the same kind.

As the valence becomes higher and higher, the effect of the extra charge on the ion becomes less and less. In the case of ferro- and ferri-cyanide ions it is practically zero. Their migration velocities are 89.6 and 90.3, respectively.

Absolute Velocities of the Ions.— By the procedure given by Kohlrausch, it is possible to calculate the velocity in centimeters per second $\left(\frac{\text{cm.}}{\text{sec.}}\right)$ with which the individual ions are driven through an aqueous solution under the influence of a given potential gradient, or potential fall, per centimeter. For the sake of simplicity let us con-

[1] Sitzungsber. d. K. Ak. d. Wiss. Wien. Math.-naturw. Kl., 61, 11 b, May, 1902. Units = Siemens; temperature = 25°.

sider two platinum electrodes, one centimeter apart, with one equivalent of negative and one of positive ions between them. Let the fall in potential from one electrode to the other be one volt. If, under these circumstances, exactly 0.001 $\underline{Q}$ ($Q = 96{,}540$) coulombs of electricity pass through a cross section of the solution in one second, and if the positive and negative ions migrate with the same velocity, then each ion travels through a distance of 0.0005 centimeter during this time, or possesses the velocity 0.0005. Since 0.001 $\underline{Q}$ coulombs pass though the cross section, 0.001 of an equivalent of an ion separates at each electrode. Moreover, 0.001 of an equivalent of ions must pass through every cross section of the solution, of which quantity 0.0005 of an equivalent are positive, going toward the cathode, and 0.0005 negative, going toward the anode. Therefore 0.0005 of an equivalent of ions is brought up to each electrode. In other words, the ions, which at the beginning of the electrolysis were 0.0005 of a centimeter from the electrode to which they were to migrate, would just reach the electrode in one second. This gives the desired absolute velocity of the ions. In the case under consideration, the sum of the distances traversed by the positive and the negative ions in one second is equal to 0.001 of a centimeter.

The quantity of electricity which has passed through the solution in one second (*i.e.* the current C in the amperes) divided by Q, or 96,540, gives, under the conditions mentioned, the velocity of the ions in centimeters per second, or, otherwise expressed,

$$\frac{\text{Current}}{96540} = \text{Velocity of the ions in centimeters per second.} \qquad (a)$$

Thus in the above case,

$$\frac{96.540}{96540} = 0.001 \text{ centimeter per second.}$$

The relation between the current, fall in potential between the electrodes, resistance, and conductance is as follows: —

$$\text{Current} = \frac{\text{Potential-fall}}{\text{Resistance}},$$

and

$$\text{Conductance} = \frac{1}{\text{Resistance}}.$$

Combining these equations, the following is obtained: —

$$\text{Current} = \text{Potential-fall} \times \text{Conductance}.$$

Since the potential-fall is one volt, it follows that —

$$\text{Current} = \text{Conductance (express in reciprocal ohms)}.$$

But there is one equivalent of the electrolyte between the two electrodes. Therefore, in this case, the conductance measured is the equivalent conductance, and the above equation becomes —

$$\text{Current} = \text{Equivalent conductance.}$$

By substituting this value of the current in equation (*a*), the following is obtained: —

$$\frac{\text{Equivalent conductance}}{96540} = \text{Total velocity of the ions.} \qquad (b)$$

If the two ions do not move with the same velocity, they share the above total velocity in proportion to their individual migration velocities.

A numerical example will make this discussion clearer. The equivalent conductance of an infinitely dilute solution of potassium chloride at 18° *t* is equal to 130.0 reciprocal ohms. Hence, according to equation *b*, —

$$\text{Total velocity of } K^{\cdot} + Cl' = \frac{130.0}{96{,}540}, \text{ or } 0.001346 \text{ cm. per second.}$$

But for potassium chloride, $\frac{v_c}{v_a} = \frac{64.6}{65.4}$.

Hence the two ions $K^{\cdot}$ and Cl' share the total velocity in the ratio 64.6 : 65.4. Accordingly, for the potential gradient of one volt per centimeter,

$$\text{Velocity of } K^{\cdot} = 0.000669 \text{ cm. per second,}$$

and

$$\text{Velocity of } Cl' = 0.000677 \text{ cm. per second,}$$

in a solution of infinite dilution.

The absolute migration velocities $v_{c\infty}$ and $v_{a\infty}$ of a number of ions at *infinite dilution* in water solution at 18° *t*, calculated from the most recent values of the migration velocities expressed in units of conductance (see page 93), are given in the following table: —

Cations	Velocity $\frac{\text{sec.}}{\text{cm.}}$	Anions	Velocity $\frac{\text{sec.}}{\text{cm.}}$
$K^{\cdot}$	0.000669	Cl'	0.000677
$NH_4^{\cdot}$	0.000667	NO_3'	0.000640
$Na^{\cdot}$	0.000450	ClO_3'	0.000570
$Li^{\cdot}$	0.000346	OH'	0.001802
$Ag^{\cdot}$	0.000559		
$H^{\cdot}$	0.003294		

The migration velocities of ions is less in solutions in which the dissociation is incomplete. According to the above discussion, the sum of the migration velocities of positive and negative ions, in such solutions, is given by the expression,

$$\frac{\Lambda_D}{96540},$$

when Λ_D represents the equivalent conductance of the electrolyte in question at the dilution D. Since, in such cases, only a portion of the electrolyte takes part in the migration, the absolute migration velocity obtained upon the assumption that the entire equivalent of ions migrates is too small. For the individual ions, in sufficiently dilute solutions, the following equations hold: —

$$u_a = x(u_a)_\infty, \text{ and } u_c = x(u_c)_\infty.$$

Here, u_a and u_c represent the migration velocities of the anion and cation respectively, in a solution in which the degree of dissociation is equal to x.

It is of interest to note, that it is possible to verify the above calculated values of the absolute migration velocities of the ions by direct experiments. Such experiments have been carefully carried out by Whetham, Masson, and later by Abegg and Steele,[1] following the method given by Lodge. The results obtained are in remarkable agreement with the calculated values. In a preliminary experiment, Lodge measured roughly the migration velocity of hydrogen ions in the following manner: He brought an acid solution into contact with a solution of sodium chloride made red with alkaline phenolphthalein and solidified in gelatine as shown in the accompanying diagram [Figure 32]. An electric current was then passed

FIG. 32

from the acid solution through the salt solution, in such a direction that the hydrogen ions entered the colored gelatine at a. As these ions slowly penetrated this solution of sodium chloride in jelly they

[1] *Ztschr. phys. Chem.*, 11, 220 (1893); *Ztschr. phys. Chem.*, 29, 501 (1899); *Ztschr. Elektrochemie*, 7, 618 (1901); *Ztschr. phys. Chem.*, 40, 699 and 737 (1902).

destroyed the red color of the indicator. Hence, by measuring the rate of progress of this decoloration, *i.e.* the time required for the moving boundary between the colored and colorless parts of the solution to reach *b* (a known distance from *a*), Lodge obtained the actual velocity of the hydrogen ions. He did not, however, correctly interpret his results.

Whetham improved the method used by Lodge, and determined the migration velocities of complex copper ions in ammoniacal solution of chlorine, and of bichromate (Cr_2O_7'') ions. He placed two dilute solutions of the same specific conductance, one of which was colorless and the other colored (such as, for example, solutions of potassium carbonate and potassium bichromate) in an upright tube, the one of least density above the other. If this is carefully done, a sharp boundary may be obtained between colored and colorless solutions, and, when an electric current is passed through the solution in such a direction that the colored ions are migrated into the colorless solution, their velocity may be obtained by measuring the rate of movement of this boundary. The fall in potential per centimeter, or the potential gradient, must be measured at the same time, for the velocity of the ions varies directly with it.

It has been shown by Abegg and Steele that the method employed by Whetham is also applicable to solutions, which, although colorless, refract a beam of light to different degrees, thus making it possible to follow the movement of the boundary between the two solutions. They determined the migration velocity of various ions at different dilutions of the electrolyte used, and found that the results obtained agree well with the requirements of the theory. As the dilution increases, the migration velocity increases and approaches the values calculated for infinite dilution.

In a way these experiments on the migration velocities are a continuation and extension of those performed by Davy and described on page 38. Davy was, however, prevented from attaining the real object of them by erroneous assumptions regarding ions.

In this connection it may be mentioned that Whitney and Blake [1] found that negative colloidal suspensions of gold, platinum, ferricferrocyanide, and a suspension of microscopic quartz particles, possess an initial velocity of migration of 0.0004 to 0.0005 centimeter per second, *i.e.* nearly equal to that of ClO_3' ions.

Electrolytic Frictional Resistance. — Having calculated the absolute migration velocities of the ions, the frictional resistance, or the

[1] *J. Am. Chem. Soc.*, **26**, 1339 (1904).

force required to drive them through a solution,[1] is easily obtained. The mechanical energy or work expended is given by the equation,

$$E_m \text{ or } W_m = \text{Force} \times \text{Distance}.$$

If the force required to drive one equivalent of a given kind of ions through a solution with a unit velocity of one centimeter per second is $\underline{F}$, then the force required to drive the same quantity with a velocity U centimeters per second is equal to $\underline{F}U$. By substitution of these values in the above equation, we obtain

$$E_m \text{ or } W_m = \underline{F}U \times U.$$

The electrical energy E_e, or electrical work, is represented by the equation,

$$E_e \text{ or } W_e = \text{Volts} \times \text{Coulombs} = \text{Volts} \times \text{Amperes} \times \text{Seconds}.$$

By substitution of the numerical values in this equation, the following is obtained: —

$$E_e \text{ or } W_e = 1 \times 96540\ U = 984515\ U \text{ kgm. cm.}$$

By placing the mechanical work equal to the electrical work, —

$$\underline{F}U \times U = 984515\ U;$$
$$\underline{F} = \frac{984514}{U}.$$

If one equivalent of ions be represented by Eq, then for one gram of the ions,

$$\underline{F}' = \frac{984515}{U \times Eq}$$

The value of this force for hydrogen ions in a solution in which complete dissociation has taken place has, for example, been calculated to be equal to 299×10^6 kilograms. This enormous value of the force is in agreement with the results of other calculations, and may be accounted for by the extreme state of division of the gram of hydrogen ions. According to the calculations made by Planck, one atomic weight in grams of an elementary substance consists of 0.617×10^{24} atoms. One atom of hydrogen, then, weighs 1.63×10^{-24} grams, and is charged with 15.65×10^{-20} coulombs of electricity. This charge may be considered as an elementary quantity of electricity.

[1] *Wied. Ann.* **50**, 385 (1893).

The Limited Applicability of the Ostwald Dilution Law. Empirical Rules.— It is evident from a consideration of its derivation that the equation,

$$\frac{\mathrm{K}_D^2}{\mathrm{K}_\infty(\mathrm{K}-\mathrm{K}_{\infty D})D} = K_d,$$

which is an expression of Ostwald's Dilution Law, is applicable only in the case of binary electrolytes. From the fact that slightly dissociated acids of other types, such as the di- and tri-basic acids, behave on dilution according to the requirements of the above equation, it follows that, at first, only one hydrogen atom separates as a positive ion, leaving the others combined in the univalent negative ion, as represented in the equation,

$$H_3A \rightleftarrows H^{\cdot} + H_2A'.$$

On continued dilution, the other hydrogen atoms begin to separate appreciably in the form of ions, and simultaneously the negative ions from which they separate increase their valences. This is evident from the equation,

$$H_2A' \rightleftarrows H^{\cdot} + HA''.$$

Experiments have not been made to determine dissociation constants for tertiary electrolytes; moreover, as will be seen from the following discussion, they probably would not be very successful.

It has been found that the above dissociation equation does not hold for highly dissociated binary electrolytes, such as the neutral salts, the mineral acids, and the inorganic bases. Consequently the relations formerly deduced for highly dissociated electrolytes from the dissociation equation can only be considered as mere approximations. Regarding the cause of this inapplicability of the equation opinions still differ widely.[1]

The following empirical equation holds well over a wide range of temperature, for salts which dissociate into monovalent or into monovalent and polyvalent ions, at concentrations between the values 0.001 and 0.2 normal:—

$$\frac{C(1-x)}{(Cx)^n} = \text{Constant},$$

where C represents the concentration of the solution, x the degree of dissociation, and n a numerical value which varies from 1.43 to 1.56.

[1] See, for example, *Jahrbuch d. Elektrochemie*, 8, 102 (1902), and A. A. Noyes, *Technology Quarterly*, 17, No. 4 (December, 1904).

For salts which dissociate into monovalent or into monovalent and polyvalent ions, the following simpler equations hold between the concentrations 0.0005 and 1 normal: —

$$1 - x = \text{Constant} \times C^{\frac{1}{3}},$$

or

$$1 - x = \text{Constant} \times (Cx)^{\frac{1}{3}}.$$

Hence the undissociated part of a salt, as determined by conductivity measurements, is proportional to the cube root of the total concentration of the salt, or to the cube root of its ion concentration.

An empirical rule, expressing the change of equivalent conductance of neutral salts with the dilution, has been discovered by Ostwald. By means of this rule, it is possible to calculate the basicity of an acid, and also the value of its equivalent conductance at infinite dilution. It is of great service in the case of salts which undergo hydrolysis to a large extent at moderately high dilutions.[1] Ostwald found that the equivalent conductance of the sodium salts of all monobasic acids increases ten units,[2] of all dibasic acids twenty units, and of all tribasic acids thirty units, between the equivalent dilutions 32,000 and 1,024,000 cubic centimeters. If the increase in equivalent conductance between these two dilutions be represented by Δ, and the basicity of the acid by B, then the rule is expressed by the equation,

$$B = \frac{\Delta}{10}.$$

The following values for Δ and $\frac{\Delta}{10}$ have been obtained: —

Sodium Salt of	Δ	$\frac{\Delta}{10}$
Nicotinic acid	10.4	1.04 (approx. 1)
Chinoline acid	19.8	1.98 (approx. 2)
Pyridine tricarbonic acid	31.0	3.10 (approx. 3)
Pyridine tetracarbonic acid	40.4	4.04 (approx. 4)
Pyridine pentacarbonic acid	50.1	5.01 (approx. 5)

On the other hand, from the value of this difference Δ of an acid of known basicity, an indication may be obtained of the presence or absence of hydrolysis. In the case of a salt of a very weak acid, as, for example, potassium cyanide, as the dilution increases the cyanide ions combine to a certain extent with the hydrogen ions of the water

[1] *Ztschr. phys. Chem.*, 1, 109 and 529 (1887); 2, 901 (1888).

[2] The values used on pages 126 and 127 are expressed in reciprocal Siemens units.

(see next section), forming undissociated hydrocyanic acid. The cyanide ions which thus disappear are replaced by hydroxyl ions from the water. This reaction between the salt and water, or the hydrolysis, is represented by the equation,

$$K^{\cdot} + CN' + H^{\cdot} + OH' \text{ (from water)} \rightleftarrows \underline{HCN} + K^{\cdot} + OH'.$$

The final result, then, of the dilution is that the number of hydroxyl ions, instead of that of the cyanide ions, has been increased. Since the migration velocity of hydroxyl ions is far greater than that of cyanide ions, the equivalent conductance of potassium cyanide increases more rapidly with increasing dilution than would be the case in the absence of hydrolysis, and, consequently, the value of the above difference Δ is abnormally great. An analogous process takes place in the case of a salt of a strong acid and a weak base, with the exception that, instead of an undissociated acid and hydroxyl ions, an undissociated base and rapidly migrating hydrogen ions are formed.

Finally, for neutral salts which dissociate to a large degree the following relation has been found to exist: —

$$\Lambda_\infty - \Lambda_D = v_a \times v_c \times K;$$

or

$$\Lambda_\infty = (v_a \times v_c \times K) + \Lambda_D,$$

when Λ_D is nearly equal to Λ_∞. In these equations, v_a and v_c represent the valency of the anion and cation, respectively, and K is a constant for all electrolytes which is dependent on the dilution. Having determined the value of the constant at different dilutions once for all for a single electrolyte of known equivalent conductance at infinite dilution, it is possible to calculate the latter equivalent conductance for any other electrolyte from a knowledge of the valences of its ions and its equivalent conductance, at any dilution for which the constant is known. If the product $v_a \times v_c \times K$ is represented by p_D, when D is the equivalent dilution of the solution in cubic centimeters, then

$$\Lambda_\infty = p_D + \Lambda_D.$$

$v_a \times v_c$	p_{6400}	$p_{12,800}$	$p_{256,000}$	$p_{512,000}$	$p_{1,024,000}$
1	11	8	6	4	3
2	21	16	12	8	6
3	30	23	17	12	8
4	42	31	23	16	10
5	53	39	29	21	13
6	(60)	48	36	25	16

In the preceding table are given the values found by Bredig for p_D for different values of the product of the valencies of the ions and for different dilutions at 25° t.

The following relation, which was first noted by Bodländer and Storbeck,[1] can often be conveniently used: —

$$x_{(1+n)} = x^n_{(1+1)},$$

when x_{1+n} represents the degree of dissociation of a salt which forms univalent and n-valent ions, and x_{1+1} that of a salt which dissociates only into univalent ions. This equation holds when salts of the same base are compared at the same equivalent concentration. Thus, if the salts potassium chloride and potassium ferrocyanide be compared at the same dilution,

$$x_{K_4Fe(CN)_6} = x^4_{KCl}.$$

It may be mentioned, in conclusion, that the fact, already noticed, that the migration velocities are dependent chiefly upon the number of atoms contained in the ion, may be used in order to obtain the value of the equivalent conductance of compound ions at infinite dilution. If it is known, for example, that the anion of a certain acid contains eighteen atoms, its equivalent conductance at infinite dilution may be considered to be equal to that of another anion of the same number of atoms, without introducing any considerable error. The same reasoning may be applied to the temperature coefficients of the conductance of individual ions.

The Conductivity and Degree of Dissociation of Water. — Thus far it has been assumed that the observed conductance of aqueous solutions is due entirely to the dissolved substance, or solute, and that the water itself possesses no conductance. Strictly speaking, however, this is not true, for the water dissociates, though to an extremely slight degree, into hydrogen and hydroxyl ions which take part in the conductance with whatever other ions there may be present. For all ordinary measurements of the conductance of solutions, the conductance of the pure water is entirely inappreciable. On the other hand, the impurities usually found in water, such as traces of salts, acids, or bases, which are removed only with great difficulty, may cause a considerable error in the conductance determinations in the case of dilute solutions. When such solutions are being investigated, it is necessary to determine the conductivity of the water used, and to apply the value obtained as a correction in the final results.

For a number of years Kohlrausch expended a great deal of effort

[1] *Ztschr. anorg. Chem.*, **39**, 201 (1904).

in determining the actual conductance of pure water. For water which was prepared and purified with the greatest care, he found the following values for the specific conductance, or conductivity:[1]—

Temperature (t)	Specific Conductance
0°	0.01×10^{-6}
18°	0.038×10^{-6}
50°	0.17×10^{-6}

"One millimeter of this water at 0° possessed a resistance equal to that of forty million kilometers of copper wire of the same sectional area, or a length of wire capable of encircling the earth a thousand times."

For reasons not necessary to give here, it is probable that this experimentally found value is very near the actual value of the conductivity of pure water. Given this value, the degree of dissociation of water can easily be calculated.

The above table states that the conductance of a centimeter cube of this water at 18° is equal to 0.038×10^{-6} reciprocal ohms. Consequently the conductance of one liter of it between electrodes one centimeter apart is 10^3 times greater than this value, or equal to 0.038×10^{-3}. If there were present, in this quantity of the water, one equivalent of hydrogen and one of hydroxyl ions, the conductance would have been equal to 492 reciprocal ohms, since, as has already been explained, the conductance of one equivalent of hydrogen ions between electrodes one centimeter apart is equal to 318, and that of the same quantity of hydroxyl ions, under the same conditions, 174 reciprocal ohms. If the conductance had been found to be equal to 492 reciprocal ohms, the water would have been 1/1 normal in respect to hydrogen and hydroxyl ions. It was, however, found to be 0.038×10^{-3} reciprocal ohms. Hence the concentration of these ions in the water is equal to $\frac{0.038 \times 10^{-3}}{492}$, or 0.77×10^{-7}, normal, or, otherwise expressed, one gram of hydrogen and seventeen grams of hydroxyl ions are present in about thirteen million liters of water.

Supersaturated Solutions. — The idea has been prevalent for a very long time, and has not even yet disappeared, that supersaturated solutions must behave in a manner characteristically different from saturated and unsaturated solutions. Conductivity measurements

[1] Kohlrausch and Heydweiller, *Ztschr. phys. Chem.*, 14, 317 (1894).

have, however, shown that supersaturated solutions possess no peculiar properties not manifested by other solutions. If, for example, the conductivity of a solution of a salt, whose solubility increases rapidly with rising temperature, be measured at a series of temperatures varying from those at which the solution is supersaturated to those at which it is unsaturated, it will be found that the change of conductivity with the temperature is perfectly regular throughout. If the results thus obtained be plotted on a coördinate system, it will be found that a regular curve results which gives no evidence of the passage of the solution from the supersaturated to the saturated, and finally to the unsaturated, state. If supersaturated solutions were qualitatively different from ordinary solutions a sudden change in the slope of the curve would have been observed at the saturation temperature.

Temperature Coefficient. — According to Kohlrausch, the change in conductivity with the temperature is nearly linear, and may be expressed, often between wide temperature limits, by the following equation: —

$$(\Delta^{K}_{1^\circ}) = \frac{1}{K_0} \times \frac{K_2 - K_1}{t_2 - t_1}.$$

In this equation K_2 and K_1 are the conductivities at the temperatures t_2 and t_1 respectively; (ΔK_{1°) is the temperature coefficient, which gives the change of conductance, expressed as a fraction of the conductivity, K_0, at a given temperature, for a change in temperature of one degree. Generally 18° is chosen as the given temperature. The above equation may then be written as follows: —

$$(\Delta K_{1^\circ}) = \frac{1}{K_{18^\circ}} \times \frac{K_2 - K_1}{t_2 - t_1}.$$

It has been found that, in the case of all well investigated electrolytes which dissociate to a high degree into univalent ions, the temperature coefficient is the greater the smaller the value of the equivalent conductance. From this fact Kohlrausch deduced the following principle:[1] *The temperature coefficient of univalent ions is a function of their mobility.* That is to say, *the greater the migration velocity the less is the temperature coefficient.* It follows from this that the ratio of the mobilities of any two ions approaches unity as the temperature increases, which is in agreement with the

[1] Sitzungsber. der königl. Pr. Akad. der Wiss. Physik. Mathem. Kl., **26**, 572 (1902).

statement made on page 76 that the transference numbers approach the value 0.5 with increasing temperature.[1]

The magnitude of the temperature coefficient at ordinary temperatures is shown by the values for dilute solutions given in the following table:—

Dilute Solute	Temperature Coefficient
Salts	0.020 to 0.023
Acids	0.009 to 0.016
Bases	0.019 to 0.020

A temperature difference of one degree thus changes the value of the conductivity by from one to two and a half per cent, from which the importance of making conductivity measurements only at constant temperatures is at once evident.

As the concentration of the solution is increased, the temperature coefficient at first decreases and then increases slightly.

With the aid of the expression,

$$v_t = v_{18}\,(1 + \alpha\,(t - 18) + \beta\,(t-18)^2),$$

the migration velocity of an ion at temperatures not far from 18° t, v_t can be calculated if the values α, β, and v_{18} be known for this ion. A table of values of v_{18} is given on page 93. In the following table are given the values of α and β calculated by Kohlrausch[2] from experimental data:—

Ion	α	β	Ion	α	β
H	0.0154	− 0.000033	F	0.0232	+ 0.000094
OH	179	+ 08	IO_3	233	096
NO_3	203	47	$C_2H_3O_2$	236	101
I	206	52	½ Ba	239	106
ClO_3	207	54	½ Cu	240	107
Cl	215	67	½ Pb	244	114
Rb	217	69	Na	245	116
K	220	75	½ Mg	255	132
NH_4	223	79	½ Zn	256	133
½ SO_4	226	84	Li	261	142
Ag	231	93	½ CO_3	269	155
½ Sr	231	93			

[1] Further particulars may be found in the recent comprehensive investigation of Jones and West, *Am. Chem. J.*, 34, 357 (1905).

[2] *Sitzungsber.*, 42, 1031 (1901).

It may further be mentioned that conductivity measurements have recently been carried out at very high temperatures (to above 300°).[1]

If it be imagined that the ions in moving through a solution must overcome a certain frictional resistance, the existence of a certain parallelism between the change of the internal friction or viscosity and that of electrical conductance of many solutions with the temperature becomes comprehensible. There is not, however, a strict proportionality between the two properties.

Finally, it is a noteworthy fact that, *in contrast to conductors of the first class, the temperature coefficient of the conductance of electrolytes is nearly always positive.* In other words, the conductivity of an electrolyte nearly always increases with increasing temperature. The conductance of a solution depends both upon the *migration velocity* and the *number* of the ions contained in it. The migration velocity itself depends upon the magnitude of the friction which the ions encounter in the water. Since the internal friction of the water diminishes with rising temperature, it may be assumed that the friction of the ions also diminishes and, as a consequence, the conductance increases. This must be the case especially with salt solutions, since, owing to the high degree of dissociation, the increase in conductance with rising temperature cannot be ascribed to any considerable extent to a change in the degree of dissociation. According to this conception of the temperature effect, a decrease in conductance with rising temperature can only take place when the effect of the diminution in the number more than compensates the effect of the increased mobility of the ions. In other words, with rising temperature a decrease in dissociation of the electrolyte must in this case take place. To many this conclusion may, at first sight, seem unjustifiable, in view of the fact that from the kinetic gas theory it would be expected that with rising temperature an increase in dissociation would take place. According to the laws and principles of energetics however, this is not at all the case, but, on the contrary, it may be predicted that in certain cases an increase in temperature must be accompanied by a decrease in dissociation. The principle of energetics applying to such changes may be stated as follows:—

If one of the factors determining the equilibrium of a system be varied in one direction, the equilibrium undergoes a change which, if it took place of itself, would be accompanied by a variation of this factor in the opposite direction.

[1] A. A. Noyes and W. D. Coolidge, *Ztschr. phys. Chem.*, **46**, 323 (1903).

If the factor temperature be varied in a chemical system, the above principle may be restated as follows:—

If a chemical system at equilibrium be heated, the equilibrium is displaced in that direction in which heat is absorbed.

Consider, for example, a saturated solution of a substance in contact with the solid substance. If the solution be heated, according to the principle of energetics, that change will take place which is accompanied by an absorption of heat, *i.e.* by a cooling effect. Consequently, if the substance dissolves (in a nearly saturated solution) with an absorption of heat, more of it will go into solution; if with an evolution of heat, some of it will precipitate out of solution.

In a similar manner, the principle may be applied to the change of the dissociation of any electrolyte with the temperature. All electrolytes which tend to become less dissociated with rising temperature, and consequently all electrolytes possessing negative temperature coefficients of the conductance, must dissociate with an evolution of heat, or, otherwise expressed, must possess a negative heat of dissociation. By heat of dissociation is meant the heat effect attending the union of ions to form an undissociated molecule, and by positive and negative heats is meant respectively the heat that is given off to or absorbed from the surroundings.

By means of direct determinations of the heat of dissociation, it is possible to test the correctness of the above conclusions.

Heat of Dissociation. — According to the dissociation theory, the process of neutralization of a strong base with a strong acid consists solely in the combining of the hydrogen ions of the acid and the hydroxyl ions of the base to form undissociated water molecules. It has already been shown that the degree of dissociation of water is very small. Consequently the product of the concentrations of the hydrogen and the hydroxyl ions must be extremely small. Now according to the law of mass action, whenever hydrogen and hydroxyl ions are brought together, combination must take place as required by the equation,

$$\frac{C_{H'} \times C_{OH'}}{C_{H_2O}} = K_w.$$

Since, in an aqueous solution the concentration of the undissociated water is very great compared with that of the hydrogen and hydroxyl ions, it may be considered a constant. The above equation may then be written as follows,

$$C_{H'} \times C_{OH'} = K_w.$$

Since even in pure water sufficient hydrogen and hydroxyl ions are always present to satisfy this equation, and as the value of this product cannot be exceeded, it follows that all hydrogen and hydroxyl ions brought into water must disappear. Now before mixing an alkali with an acid solution, we have in one case metal and hydroxyl ions and in the other acid and hydrogen ions, as may be illustrated by sodium hydroxide and hydrochloric acid. In this case the following ions are present in the two solutions, respectively: —

$$Na^{\cdot} \text{ and } OH'; \quad H^{\cdot} \text{ and } Cl'.$$

After mixing the acid and alkali solutions, the ions of the metal and of the acid radical are still present and free in the solution, constituting a highly dissociated salt. *They have taken no part in the process of neutralization.* In the case of sodium hydroxide and hydrochloric acid, only sodium and chlorine ions are present after mixing the two solutions, constituting sodium chloride in the dissolved state. Hence the real reaction which has taken place is represented by the equation

$$H^{\cdot} + OH' = H_2O.$$

It is because of the fact that the ions of the metal and those of the acid radical take no part in the process of neutralization that the value of the heat of neutralization is the same for all highly dissociated acids and bases, being in each case the heat of the union of hydrogen and hydroxyl ions to form undissociated water. This value for one equivalent of acid and base is 13,700 calories, at ordinary temperatures. Hence the above equation may be written as follows: —

$$H^{\cdot} + OH' = H_2O + 13700 \text{ calories},$$

where the ions are present in equivalent quantities.

The value **13,700** *calories then really represents the heat of dissociation of water.*

This value must not be confused with the heat evolved when *gaseous* hydrogen reacts with *gaseous* oxygen to form water.

If a partially dissociated acid be neutralized with a highly dissociated base, the heat of neutralization will be made up of the sum of two heats of dissociation, namely, that of water and that of the acid. Representing the heat of neutralization by H_n, the degree of dissociation of the acid by x, and the heat of the dissociation of the acid by H_d, then

$$H_n = 13700 - (1 - x)\, H_d \text{ calories}.$$

Hence it follows that

$$H_d = \frac{13700 - H_n}{1 - x} \text{ calories.}$$

All dissociating acids which exhibit a greater heat of neutralization than 13,700 calories have negative heats of dissociation. It has actually been found by Arrhenius[1] and later by Euler that all acids which possess a negative temperature coefficient of electrical conductivity have also negative heats of dissociation. Such acids therefore decrease in dissociation with rising temperature.

Influence of Pressure. — The influence of pressure upon the conductivity of electrolytes may be predicted from the same reasoning which explains the influence of temperature. By means of a change in pressure a change may be produced in the concentration of the solution, the friction of the ions, and the dissociation of the electrolyte. Eliminating the change in concentration, which may be applied as a correction in the calculation of the final results, experiment shows that, in general, the conductivity of dilute solutions of highly dissociated electrolytes increases with increasing pressure. This may be ascribed to a diminution in the friction of the ions with the water. This is in agreement with the fact that the internal friction or viscosity of water decreases with increasing pressure. Therefore, as in the case of the temperature effect, there exists here also a parallelism between the change in conductivity and the change in internal friction.

In the case of electrolytes which are but partly dissociated, the effect of pressure upon the degree of dissociation must also be taken into consideration. This may be obtained from the volume change during dissociation, just as the effect of temperature change was obtained from the heat evolved or absorbed during dissociation, *i.e.* the heat of dissociation. If the formation of ions is accompanied by a diminution in volume, then an increase in pressure is accompanied by an increase in the degree of dissociation. This follows from the law stated on page 132 expressing the change in equilibrium caused by a change in one of its factors, since an increase in pressure is accompanied by a decrease in volume, and this change in dissociation, taking place of itself, is accompanied by a decrease in volume. As a matter of fact, the dissociation of many moderately dissociated acids is accompanied by such a decrease in volume; and corresponding to this, the increase in volume during neutralization with a strong base is less for these acids than for acids which

[1] *Ztschr. phys. Chem.*, 4, 96 (1889); 9, 339 (1892).

are nearly completely dissociated. This is analogous to the above consideration of the heat of dissociation.

It is a necessary consequence from the investigations of Fanjung[1] that the conductivity of such acids should increase with rising pressure to a greater extent than that of highly dissociated electrolytes, especially in the case of their sodium salts. This is in complete agreement with the above explanations.

Mixed Solutions: Isohydric Solutions. Application of Electrical Conductivity to Chemical Analysis. — If the conductivities of two solutions and of a mixture of equal volumes of the two solutions are determined under the same circumstances, it will not, in general, be found that the latter value is equal to the average of the other two, excepting in the case of completely dissociated solutions. On mixing solutions of sodium chloride and potassium nitrate, for example, some undissociated potassium chloride and sodium nitrate must result, whereby the relations are complicated.

Solutions which, when mixed, do not mutually affect the individual conductivities, have been called by Bender "*corresponding solutions*," and by Arrhenius, who investigated acid solutions chiefly, "*isohydric solutions*." Two solutions are now said to be isohydric when the concentration of the common ion is the same in each solution. No change in dissociation occurs, then, upon mixing them. This will be evident from the following discussion: —

Consider, for example, one solution to be of acetic acid and the other of salicylic acid. For the solution of acetic acid, according to the law of mass action, we have the equation,

$$\frac{C_i \times C_i}{C_{HAc}} = \frac{C_i^2}{C_{HAc}} = K_{HAc},$$

and for salicylic acid, the equation,

$$\frac{C'_i \times C'_i}{C_{HSal}} = \frac{C'^2_i}{C_{HSal}} = K_{HSal},$$

in which C_{HAc}, C_{HSal}, C_i and C'_i represent the concentrations, in the respective solutions, of the undissociated acetic acid, the undissociated salicylic acid, each ion in the acetic acid solution, and each ion in the salicylic acid solution. Since the solutions are isohydric, and hence are of equal concentration in respect to hydrogen ions,

$$C_i = C'_i.$$

If now one liter of the acetic acid solution be mixed with four liters

[1] *Ztschr. phys. Chem.*, 14, 673 (1894).

of the salicylic acid solution, the contraction in volume is negligible for such dilute solutions, and the resulting concentrations of the various constituents in the mixed solution are as follows: —

Hydrogen ions	$= C_i$ or C'_i (unchanged).
Acetate ions (CH_3COO')	$= \frac{1}{5} C_i$.
Undissociated molecules of acetic acid	$= \frac{1}{5} C_{HAc}$.
Salicylate ions (C_6H_3OCOO')	$= \frac{4}{5} C'_i$.
Undissociated molecules of salicylic acid	$= \frac{4}{5} C_{HSal}$.

By substitution of these new values in the above equations we obtain, for acetic acid in the mixture,

$$\frac{C_i \cdot \frac{C_i}{5}}{\frac{C_{HAc}}{5}} = K_{HAc},$$

or

$$\frac{C_i^2}{C_{HAc}} = K_{HAc};$$

and for the salicylic acid in the mixture,

$$\frac{C'_i \cdot \frac{4\,C'_i}{5}}{\frac{4\,C_{HSal}}{5}} = K_{HSal},$$

or

$$\frac{(C'_i)^2}{C_{HSal}} = K_{HSal}.$$

Therefore upon mixing the two solutions no change in dissociation should take place, since the requirements for equilibrium between the ions and the undissociated molecules in each case remain satisfied. Finally, it is evident that this is still true whatever the volume of the one solution may be which is mixed with a given volume of the other; and, further, that when two solutions are isohydric in reference to a third solution, they are also isohydric in reference to each other.

From what has just been said, it may be concluded that solutions of a chloride, or of a bromide, etc., of the same metal, or of nitrates of closely related metals, of the same equivalent concentration, are nearly isohydric, since they are dissociated to nearly the same extent. Hence the conductivity of a mixture of such solutions is very nearly equal to the average of the conductivities of the individual solutions. Upon this fact may be based a method of quantitative chemical analysis. If, for example, the conductivities of two solutions of potassium chloride and potassium bromide of equal percentage-con-

centration are K and K', respectively, then the conductivity of a mixture of these solutions K'' is given by the equation —

$$\mathrm{K}'' = m\,\mathrm{K} + (1-m)\,\mathrm{K}',$$

when m and $1-m$ represents the quantity of potassium chloride and of potassium bromide, respectively, contained in a unit quantity of the mixture. When the value of K'' is determined, the value of m is easily obtained from the above or the following equation: —

$$m = \frac{\mathrm{K}' - \mathrm{K}''}{\mathrm{K}' - \mathrm{K}}.$$

Since here only conductivity ratios are involved, it is evident that the conductivity measurements may be expressed in any system of units without changing the value of m. It is most convenient to express these values in terms of the conductivity of a simple solution. The inaccuracy of m increases with the differences between K and K'.

In general, it is best to ascertain whether or not the conductivities of any two solutions in question are in fact additive in a mixture of them by means of measurements carried out with known mixtures; for two other factors now to be mentioned may exert a disturbing influence. There may be a complex compound formed when the two solutions are mixed, in which case the equations deduced above no longer apply. The fact that the conductivity of the mixture is not the average of the conductivities of the constituent solutions may even serve to detect the presence of such complex compounds. Secondly, the nature of the solvent may be changed by the mixing of the two solutions, resulting in a change in the degree of dissociation and in the internal friction which the ions must overcome during migration. For instance, potassium chloride is dissociated to a greater extent when dissolved in pure water than when dissolved in a mixture of water and acetic acid containing a considerable portion of the latter liquid. (See later.) For the same reason, the addition of considerable quantities of acetic acid or of any other substance may change the conductivity of an electrolyte.[1]

Finally it should be remembered that, as a matter of fact, the requirements of the law of mass action are not always realized. The following empirical rule, which is of wide applicability when no complex compounds are formed, is therefore of considerable value. *The conductivity and the freezing-point lowering of a mixture of salts having one ion in common are those calculated under the assumption that the degree of ionization of each salt is that which it would*

[1] See *Ztschr. phys. Chem.*, 40, 222 (1902).

have if it was present alone at such an equivalent concentration that the concentration of either of its ions is equal to the sum of the equivalent concentrations of all of the positive or negative ions present in the mixture.[1]

Assuming that a mixed solution of sodium chloride and sodium sulfate is 0.1 normal in respect to the first salt, 0.2 normal in respect to the second salt, and 0.18 normal in respect to the common positive ion (or to the negative ions), then according to the above rule the degree of dissociation of each of these salts in the mixture is the same as it would be in pure water when its ion concentration is 0.18 normal.

In explaining this further, it is recalled that the following equation holds for a single salt dissolved in water (see page 126): —

$$1 - x = K(xC)^{\frac{1}{2}}.$$

Applying this equation to each of the salts in the above mixed solution, we have,

$$1 - x_1 = K_1(x_1C_1 + x_2C_2)^{\frac{1}{2}}, \text{ and } 1 - x_2 = K_2(x_1C_1 + x_2C_2)^{\frac{1}{2}}.$$

The concentration of the common ion of the mixed solution, $x_1C_1 + x_2C_2$, is here the concentration of the positive or negative ions of each individual salt in the simple water solution. Since K_1 and K_2 may be known from conductivity measurements in the case of the individual salts, and since naturally the concentrations of the two salts C_1 and C_2 are known, the values x_1 and x_2 may be found. This may best be accomplished by repeated trials until a satisfactory approximation is obtained. The equivalent conductance of the mixture is then given by the equation,

$$\Lambda_D = x_1\Lambda_{1\infty}(C_1D) + x_2\Lambda_{2\infty}(C_2D).$$

where (C_1D) and (C_2D) represent the fractions of an equivalent of the two salts, respectively, which are present in a volume D of the mixture. The sum of the two values is equal to unity. It follows from this that the conductivity, or specific conductance, is given by the equation,

$$\kappa = x_1\Lambda_{1\infty}C_1 + x_2\Lambda_{2\infty}C_2.$$

If the empirical rule stated above is valid, then the value of the conductivity of the mixed solution calculated from the above equation must agree with the experimentally determined values.

It should be added that conductivity measurements have been

[1] A. A. Noyes, *Technology Quarterly*, 17, 301 (December, 1904).

used in chemical analysis in other cases, namely, in the determination of the solubility of salts which are but slightly soluble in water, as carried out by Hollemann,[1] Kohlrausch, and F. Rose. The solubilities of such salts can be determined by ordinary chemical methods only with great difficulty.

If the solution is so dilute that the electrolyte may be considered to be completely dissociated, then

$$\Lambda_{D_e} = \Lambda_\infty,$$

and

$$\Lambda_{D_e} = \Lambda_\infty = \frac{K_c \cdot D_e}{R_e},$$

from which the value of D_e, the volume in cubic centimeters of the saturated solution in which one equivalent of electrolyte is dissolved, may be calculated: —

$$D_e = \frac{\Lambda_\infty \times R_e}{K_c}.$$

The values of R_e and K_c, the actual resistance of the solution in the conductivity cell and the cell constant, are found by direct experiment, while that of Λ_∞ is often obtained by calculation. The value of D_e being known, the solubility is determined.

The following results have been obtained in this way: —

Salt	Temperature	Concentration of Saturated Solutions
Silver bromide . . .	21.1°	$0.57 \times 10^{-9}\ C_\infty$, or 0.107 mg. per liter
Silver iodide	20.8°	0.0035 mg. per liter

In determining the solubility of many salts, as for example of the carbonates of the alkali earths, hydrolysis must be taken into consideration (see page 126). Since the hydrolysis may be driven back by the addition of OH ions, the conductivity, not of a solution of the salt in pure water, but rather of one in a dilute alkali solution, should be measured. The true value of the solubility can then be calculated from the increase in conductivity of the alkali solution which takes place when the salt is dissolved in it.

Finally, it should be mentioned that Küster[3] has recently shown

[1] *Ztschr. phys. Chem.*, **12**, 125 (1893).

[2] *Ztschr. phys. Chem.*, **12**, 234 (1893). See also Sitzungsber. d. königl. Pr. Akademie d. Wiss. Physik. Mathem. Kl., **41**, 1018 (1901); *Ztschr. phys. Chem.*, **50**, 355 (1905).

[3] *Ztschr. anorg. Chem.*, **35**, 454 (1903); **42**, 225 (1904). This application was suggested by Kohlrausch as early as 1885. See *Wied. Ann.*, **26**, 225 (1885).

that conductivity measurements may often with advantage replace indicators in the titration of acids and bases. If, for example, 10 cubic centimeters of a 0.1 normal solution of HCl be diluted to 500 cubic centimeters and titrated with a 0.1 normal solution of NaOH, then during the titration the rapidly migrating H ions of the acid are gradually replaced by the slower Na ions, and consequently the conductivity of the acid solution gradually decreases. After all H ions have been replaced and more NaOH is added, Na and rapidly migrating OH ions are increased in the solution, and, consequently, the conductivity of the solution being titrated is also increased. Hence the end point of the titration is the point at which the conductivity reaches its minimum value. In carrying out a titration in this manner, care must be taken to insure good stirring and constant temperature.

Regularity of Ionization. Reactivity of Electrolytes. — It follows from what has already been said in regard to electrical conductivity that different substances when dissolved in water or in any other solvent often dissociate to very different degrees. The question at once arises whether the ionization of different substances follows any regular scheme. It may first be questioned whether additive relations exist, or, in other words, whether for a given atom or atom-group there always exists the same tendency or force tending to form ions. If this was actually the case, and if this tendency always appeared in the same way, the following would be observed: Given all the electrolytes with a certain negative ion arranged in the order of magnitude of their dissociations, then this order would not be changed if another negative ion was substituted throughout the series. From a study of experimentally determined facts, however, it is seen that this assumption is untenable. Thus it is found that hydrochloric acid is always dissociated to a greater extent than any metal chloride in a solution of the same normality; while acetic acid is always less dissociated than any metal acetate. Moreover, zinc, cadmium, and mercury salts are notable exceptions among salts. With the halogens these metals form electrolytes which are but slightly dissociated, and with many organic anions they form electrolytes which are largely dissociated. The degree of dissociation of the corresponding acids is in the reverse order. Up to the present, furthermore, no other simple relation concerning the regularity of ionization has been discovered.

It may, however, be stated that in general all salts dissolved in water are highly dissociated, while acids and bases show very great variations in this respect, some being highly and some but slightly dissociated.

Solutions of substances not included in these classes generally possess a small, yet by exact measurements detectable, conductivity.

If a chemical process is capable of taking place between two dissolved substances, it always takes place instantaneously if the substances are dissociated to a moderate degree. The usual reactions of analytical chemistry may be cited as examples. In other cases in which the substances are either dissociated to an extremely slight degree, or to a degree beyond our means of detection, the reactions usually, but not always, take place slowly at ordinary temperatures. Thus in the preparation of organic compounds, it is usually necessary to carry out the reactions involved at a high temperature in order to obtain a satisfactory yield without an undue expenditure of time. Nevertheless, it should not be claimed that chemical reactions can take place only when the substances involved are ionized. Such a claim is decidedly too broad and is not in harmony with facts; for undissociated substances can react with each other, and in some cases with a high velocity. This is shown in an especially striking manner by the investigation of Kahlenberg,[1] according to which, solutions of stannic chloride and of copper oleate in benzene, which were nonconductors of the electric current, when mixed immediately gave a precipitate of copper chloride with the simultaneous formation of stannic oleate.

Solvents other than Water. Relation between the Dissociating Power and the Dielectric Constant of Solvents. — Already a large number of investigations have been carried out with solvents other than water or with mixtures of various solvents. It would be natural to expect that the conceptions which have been found serviceable in the case of solutions in water could be applied directly to solutions in other solvents, keeping in mind that, according to the individual nature of any given solvent, the degree of dissociation, the migration velocity of the ions, and consequently the conductivity of a solution of a given concentration would be different. It is a noteworthy fact, however, that the behavior of non-aqueous is much more complicated than that of aqueous solutions. This is shown especially by the investigation of the conductivity of solutions of various substances in liquid sulfur dioxide made by Walden and Centnerszwer.[2] Neither the law of the independent migration of the ions, nor the law that by increasing dilution the conductance approaches a maximum value, nor, finally, the dilution law, was

[1] *J. phys. Chem.*, **6**, 9 (1902).

[2] *Ztschr. phys. Chem.*, **39**, 513 (1902), and Walden, *Ztschr. phys. Chem.*, **43**, 385 (1903).

found to hold. Molecular weight determinations carried out at the same time by the boiling-point method gave normal values for non-electrolytes, and abnormally *large* values for electrolytes, whereas abnormally *small* values would be expected. This indicates that association has taken place to a considerable extent, which in all probability takes place not only between molecules of dissolved substance, but also between these molecules and those of the solvent. Considering these circumstances, it is very fortunate for the advance of the sciences of chemistry and electro-chemistry that such complications are generally, although not always,[1] absent in the case of aqueous solutions. It is due to this fact that it has been possible to deduce simple laws from a study of such solutions.

Although for solvents other than water a single generalization under which individual results may be brought is still lacking, it is, nevertheless, important to consider some of the individual results themselves. A summary of such results compiled by Walden[2] is therefore presented here.

The solvents which have been most frequently investigated belong to the alcohol class and are given in the following table: —

Solvent	Formula	Solvent	Formula
Methyl alcohol,	CH_3OH	Trimethyl carbinol,	$(CH_3)_3COH$
Ethyl alcohol,	C_2H_5OH	Isoamyl alcohol,	$C_5H_{11}OH$
Propyl alcohol,	C_3H_7OH	Glycerine,	$C_3H_5(OH)_3$
Isopropyl alcohol,	C_3H_7OH	Benzyl alcohol,	$C_6H_5CH_2OH$
Isobutyl alcohol,	C_4H_9OH		

The conductivity of solutions of a large number of salts (including others besides those of the alkalies), acids, and bases have been determined. In the case of methyl and of ethyl alcohol, the dissociation constant of many salts were determined both by the boiling-point and by the conductivity method, without, however, obtaining anything like a satisfactory agreement. According to the results obtained by the former method, the molecular weight of the salts decreases with increasing dilution. It was not possible, however, to obtain a dissociation constant independent of the dilution, either in the case of these or of other alcohol solvents. It is a remarkable fact that only in the case of solutions of trichloracetic acid has the dilution law been found to hold.

[1] W. Biltz, *Ztschr. phys. Chem.*, 40, 185 (1902).

[2] *Ztschr. phys. Chem.*, 46, 103 (1903). An extensive list of references to the literature of the subject is also given.

Of the acids, the following have been used as ionizing substances :

Acetic acid,	Butyric acid,
Formic acid,	Benzoic acid (fused),
Propionic acid,	*o*-Nitrobenzoic acid (fused).

With the solvent formic acid, the following values were obtained at 25° :—

K_∞ (for KCl) = 60.8; K_∞ (for NaCl) = 47.5.

A considerable difference was found between the dissociation values obtained by the freezing-point method and those obtained by the conductivity method. The dilution law does not hold for these solutions.

Some of the nitriles are excellent ionizers; namely, the following lower members : —

Aceto-nitrile,	Butyro-nitrile,
Propio-nitrile,	Benzo-nitrile.

In aceto-nitrile, silver nitrate possesses an abnormally small molecular weight corresponding to electrolytic dissociation; in benzo-nitrile it possesses an abnormally large molecular weight, indicating the existence of polymerization.

Of the ketone solvents, acetone is the most interesting. The equivalent conductance of binary salts dissolved in it increases considerably with increasing dilution, without, however, attaining a maximum value. In this case also the dilution law does not hold.

Of the other groups of organic compounds which have been investigated, the following may be mentioned : —

Aldehydes,	Nitrogen bases (pyridene),
Esters,	Nitro-compounds,
Ethers,	Hydro-carbons.

It has already been shown that water possesses a conductivity of its own. Do other pure solvents, organic and inorganic, also conduct the electric current ? It has been found that the conductivity of most of the good ionizing solvents (SO_2Cl_2, SO_2, NH_3, $AsCl_3$), be they organic or inorganic, is of the same order of magnitude as that of water, varying between the limits,

$$K_{25}^{\circ} = 1 \cdot 10^{-7} \text{ to } 5 \cdot 10^{-7}.$$

Nevertheless, some solvents have been found which possess high conductivities, as will be evident from the following table : —

Solvent	Conductivity	Solvent	Conductivity
Form-amide,	$4.7 \cdot 10^{-5}$ (25°)	Nitric acid (anhydrous),	$1525 \cdot 10^{-5}$ (0°)
Acet-amide,	$29 \cdot 10^{-5}$ (81°)	Sulfuric acid (anhydrous),	$1000 \cdot 10^{-5}$ (approx.) (25°)
Acetyl acetone,	$1.6 \cdot 10^{-5}$ (25°)	Antimony trichloride,	$11.7 \cdot 10^{-5}$ (80°)
Formic acid,	$1.5 \cdot 10^{-5}$ (8.5°)		

These conductivities approach those of typical electrolytes.

There are other solvents which possess no conductivity even when salts or acids are dissolved in them. Such solvents are PBr_3, $SnCl_4$, $SbCl_5$, $SiCl_4$, and bromine.

It is interesting to note that the conductivity of pure organic (also of liquid, *i.e.* fused, inorganic) substances has been shown to be dependent on the constitution of the substance in question. The first member of homologous series possesses the highest value, which is decreased with each successive introduction of a CH_2-group. Substances containing OH- or CO-groups give the highest values of K.

If we hold to the dissociation theory, we must assume that all substances which conduct electricity electrolytically are ionized. In regard to the nature of this ionization, we can only surmise.

It is a remarkable fact, finally, that iodine, IBr, ICl, and ICl_3, when dissolved in SO_2Cl_2 conduct the electric current.

According to Thomson and Nernst[1] there exists a relation between the dielectric constant and the dissociating power of a liquid. In order to facilitate the understanding of this relation a few illustrations relating to the dielectric constant K_D and its determination will be given.

Besides the galvanic conductance, there is also a second constant by which the electrical behavior of a body is characterized. This constant is of great importance in the case of just those substances which conduct electricity galvanically very little or not at all, *i.e.* the so-called insulators or dielectrics. The dielectric constant, K_D, of a substance is proportional to the capacity of a condenser the insolating layer, or dielectrum, of which is this substance. If the capacity of the condenser in air is represented by k (although usually placed equal to unity) and its capacity in the medium in question by k_1, then the value of the dielectric constant is given by the equation,

$$K_D = \frac{k_1}{k}$$

The dielectric constant may also be defined as the factor which gives the decrease in the electrostatic attraction between two

[1] *Ztschr. phys. Chem.*, 13, 531 (1894).

charged spheres when the latter, while maintained at a constant distance from each other, are transferred from a space filled with air to one filled with the non-conducting medium being investigated.

A method for the determination of this constant which is very often used is that known as the Nernst Method.[1] It will be briefly considered.

Starting with the apparatus used in the Kohlrausch method for the determination of electrical conductivity as shown in Figure 29 and replacing the two resistances, the known and the unknown, in the Wheatstone bridge by two condensers, an apparatus is obtained with which, as had already been shown by Palaz, the capacities of the two condensers may easily be obtained in case the dielectrics are good insulators. The minimum sound is heard in the telephone only when the following relation obtains (see also page 104):—

$$R_1 : R_2 = k_2 : k_1.$$

If the resistance R_1 is made equal to the resistance R_2, the two condensers placed in air and one of them k_1 varied in a known manner until, at a value k_1', a minimum tone is heard in the telephone, then the capacities of the two condensers are equal. If now the dilelectrum to be investigated be inserted in the condenser k_2, and the condenser k_1 be again varied until the point of minimum tone in the telephone is obtained at the value k'', the dielectric constant of the substance K_D is given by the equation,

$$K_D = \frac{k_1'}{k_1''}.$$

When there is bad insulation in the condenser, no minimum sound is heard in the telephone, and the measurement of the dielectric constant cannot be carried out directly by the above method. It can, however, be determined if an auxiliary circuit be introduced, giving the other condenser a suitable conductance. In this case, a minimum tone is heard in the telephone when both the capacities and the conductances of the two condensers are equal. By means of this artifice, it is at once evident that it is possible, not only to determine the dielectric constant of substances which conduct galvanically, but also to determine at the same time the magnitude of the galvanic conductance.

The principle first stated by Nernst, expressing the relation between the dielectric constant and the dissociating power of a solvent, may be stated as follows:—

[1] *Ztschr. phys. Chem.*, **14**, 626 (1894).

The greater the dielectric capacity of a solvent, the greater is the degree of electrolytic dissociation of substances dissolved in it, when the conditions are otherwise the same.

The following consideration will make this principle clearer: The positively and negatively charged ions would unite to form electrically neutral molecules because of the electrostatic attraction which exists between them, if it were not for the action of another and opposing force the nature of which is as yet unknown. The equilibrium between these two forces gives rise to the equilibrium between the ions and the undissociated molecules, or determines the degree of dissociation. When the dielectric constant is increased, the electrostatic attraction between the ions is alone weakened, and hence the degree of dissociation is increased.

As will at once be seen, the principle stated by Nernst is well substantiated by the very recent measurements made by Walden.[1] Since a number of other interesting relations are furnished by these results, they will be considered somewhat in detail.

Walden determined the dissociating power of half a hundred solvents by dissolving in them one and the same binary salt, tetraethyl ammonium iodide, $N(C_2H_5)_4I$,[2] measuring the value of Λ over wide limits of dilution and, by calculation, extrapolating for the value of Λ_∞. In this manner he was able to calculate for the different solvents the value of the dissociation, —

$$x = \frac{\Lambda_D}{\Lambda_\infty},$$

which, for equal dilutions, is a measure of the dissociating power. He used the values so obtained in order to throw light on *the influence of chemical constitution on the dissociating power of various solvents*, and found that the dissociating power is increased by the introduction of —

a. Oxygen-containing radicals, such as the carboxyl, hydroxyl, keto, and aldehyde groups;

b. Nitrogen- and sulfur-containing radicals, such as the cyanide, sulfocyanate, isosulfocyanate, nitro, and sulfo groups; and

c. Oxygen in ring compounds, and amido groups in acid amides.

The values of x referred to a volume of 1000 liters is given in the following table in the order of the relative dissociating power for various groups combined with the methyl group.

[1] *Ztschr. phys. Chem.*, **54**, 129 (1906).

[2] For molecular weight determinations for this salt in various solvents see *Ztschr. phys. Chem.*, **55**, 281 (1906).

Name	Formula	∞ (%)
Acetic acid	$CH_3 \cdot COOH$	7
Acetyl chloride	$CH_3 \cdot COCl$	72
Acetone	$CH_3 \cdot COCH_3$	74
Methyl isosulfocyanate	$CH_3 \cdot NCN$	77
Acetaldehyde	$CH_3 \cdot COH$	84
Methyl alcohol	$CH_3 \cdot OH$	88
Methyl sulfocyanate	$CH_3 \cdot SCN$	89
Methyl cyanide	$CH_3 \cdot CN$	90
Nitro methane	$CH_3 \cdot NO_2$	92

A study of the homologous series of organic compounds has shown that, as the carbon content increases, the dissociating power decreases with greater or less rapidity in much the same way as in the case of the electrical conductance of the solvent.

We may now proceed further to the relation between the dissociating power and other physical properties, especially that of association. According to the assertions of some investigators a proportionality should exist here, and, moreover, the value of K_∞ should depend on the degree of association. But if the association factors of Ramsay and Shields be accepted, then it follows that both of these assertions are untenable. The comparison of the dissociating powers of various solvents with their dielectric constants has, however, resulted in the discovery of an important generalization. It has been found that *a direct parallelism exists between the dissociating power and the dielectric constants of solvents*, completely confirming the principle put forward by Nernst. This will be at once evident from the results given in the table on the next page.

This table gives an interesting survey of the magnitude of K_∞ for the various solvents. It will be seen that it varies from 8 to 225, the value for water, 112, occupying a middle position. From this fact it follows that it is inadmissible to draw a conclusion, as often has been done, regarding the degree of dissociation from the value of the equivalent conductance alone.

It is remarkable that in the case of several solvents the equivalent conductance does not increase with increasing dilution, but, according to the nature of the solvent and of the electrolyte, in one case it decreases regularly, while in another it varies in a periodic manner, passing through one or more minima and maxima. These phenomena are explained on the assumption of chemical interaction between the solvent and the electrolyte.

In the case of the two solvents, acetonitrile and epichlorhydrine,

	Solvent	Dielectric Constant K_D (20°)	Limited Value of K_{∞} (20°)	Degree of Dissociation D= 100	D= 1000	D= 2000	Temperature Coefficient Δ_t (0°–25°)
				(Per cent)			
	Water, H_2O	81.7	112	91	98	99	——
1.	Formamide, $HCONH_2$	84	25	93	98	98	0.044
2.	Glycolnitrile, H_2COHCN	67.9	71.5	93	98	99	0.0229–0.0219
3.	Ethylene cyanide, $(CH_2CN)_2$	57.3–61.2	35.5(60°)	90	95	96	0.025
4.	Nitrosodimethylene	53.3	95	—	(89)	(91)	0.0149–0.0144
5.	Citracon acidanhydride	39.5	22.5	82	93	94	0.041 –0.044
6.	Nitromethane, CH_3NO_2	38.2–40.4	120	78	92	93	0.0132–0.0136
7.	Furfurole	36.5–39.4	50	78[1]	91	93	0.0242–0.0254
8.	Lactonitrile	37.7	40	—	89	91	0.0303–0.0328
9.	Acetonitrile, CH_3CN	35.8–36.4	200	74	90	92	0.0103
10.	Methyl thiocyanate, CH_3SCN	33.3–35.9	96	77	89	91	0.0148
11.	Glycol, $(CH_2OH)_2$	34.5	8	78	89	—	0.092 –0.096
12.	Nitrobenzene, $C_6H_5NO_2$	33.4–37.4	40	71	88	90	0.0254–0.0245
13.	Methyl alcohol, CH_3OH	32.5–34.8	124	73	88	90	0.0151–0.0159
14.	Cyanacetomethylester	28.8	29.5	69	84	87	0.0439–0.0437
15.	Propionitrile, C_2H_5CN	26.5–27.2	165	65	84	87	0.0109–0.0112
16.	Ethyl thiocyanate, C_2H_5SCN	26.5–31.2	84.5	63	83	86	0.0149–0.0144
17.	Cyanacetoethylester	26.2–26.7	28.2	65	83	87	0.0392
18.	Benzonitrile, C_6H_5CN	26.0	56.5	61	80	84	0.0227–0.0231
19.	Epichlorhydrine	(26 ?)	66.8	60	81	85	0.0168–0.0209
20.	Ethyl acetone	25.1–26.0	79	—	83	87	0.0172
21.	Ethyl alcohol	21.7–27.4	60	54	78	82	0.0230–0.0224
22.	Acetaldehyde	28.6–21.1	180(0°)[1]	—	(84	86)	0.0082–0.0068
23.	Acetone	20.7–21.9	225	50	74	80	0.0082–0.0090
24.	Methyl isothiocyanate	17.9–19.7	134(50°)[1]	—	77[1]	—	0.0101–0.011
25.	Ethyl isothiocyanate	19.4–22.0	106	—	66	—	0.0124–0.0130
26.	Propionaldehyde	14.4–18.5	(145[1]	55	75[1])	145[1]	(0.0081–0.011)
27.	Acetic acid anhydride	17.9	76	58	79	84	0.0171–0.0177
28.	Benzaldehyde	14.5–16.9	42.5	51	73	78	0.0207–0.0224
29.	Benzyl cyanide	15.0–16.7	36	46	74	79	0.028 –0.031
30.	Acetyl bromide	16.2	114	47	73	78	0.0095
31.	Anisaldehyde	15.5	16.5	—	76	81	0.063 –0.072
32.	Acetyl chloride	15.5	172[1]	46	72	79	0.007 –0.0068
33.	Salicylaldehyde	13.9 (19.2)	25	34	55	61	0.0467
34.	Isobutyric acid anhydride	13.6	42[1]	—	66[1]	73[1]	0.018
35.	Thioacetic acid	12.8–17.3	77[1]	—	68[1]	74[1]	0.0138
36.	Benzoyl acetic acid ester	11.0–14.3	>7	—	50[1]	56[1]	0.086 –0.097
37.	Malonic acid dimethyl ester	10.3	>25	—	—	41	0.0285
38.	Isovaleric aldehyde	10.1–11.8	——	—	—	—	(0.0047–0.0123)
39.	Acetic acid	6.46	21[1]	—	(7)	(9)	(0.057 –0.060)
40.	Dimethyl sulfide, $(CH_3)_2S$	6.2	——	—	—	—	——
41.	Ethyl mercaptan, C_2H_5SH	7.95	——	—	—	—	——
42.	Aldoxime, CH_3CHNOH	3.4	——	—	—	—	——
43.	Tetranitromethane	<2.2	——	—	—	—	——
44.	Dimethyl sulfate	46.5	43	—	91	93	0.0230–0.0228
45.	Diethyl sulfate	30[1]	43	—	84	86	0.024 –0.026
46.	Asym. Diethyl sulfite, $C_2H_5SO_3$	38.6	26.4	—	94	95	0.0325–0.0327
47.	Ethyl nitrate	19.4–17.7	138 or 140	—	58(72)	67(78)	0.0105–0.0220
48.	Sym. Diethyl sulfite, $SO(OC_2H_5)_2$	16.0	76	—	50	61	0.0111–0.0133
49.	Trimethyl borate	8.0	188[1]	—	(9)	(12)	0.0068

[1] Approximate.

in which a considerable number of electrolytes have been investigated, it has been found that the law of the independent migration of ions (Kohlrausch's law) is valid.

From a further consideration of the values of K_∞ given in the table it is evident that there also exists a certain relationship between them and the chemical constitution of the solvent. For example, in homologous series the value decreases with increasing carbon content. A relationship between the value of K_∞ and the physical properties of the solvent has not been found. On the other hand, it has been found that the product of K_∞, the equivalent conductance at 25°, and the temperature coefficient for the conductance of very dilute salt solutions varies about the same value in the case of solutions differing widely from each other. Otherwise expressed,

$$K_\infty \cdot \Delta_t K(0°\text{–}25°) = 1.30 \text{ (approx.)},$$

where

$$\Delta_t K(0°\text{–}25°) = \frac{1}{K_{0°}} \cdot \frac{K_{25°} - K_{0°}}{25}.$$

The variation from the value 1.30 is considerable only in the case of a few substances.

There is also a numerical relationship between the dielectric constants and the dilutions in various solvents which give the same degree of dissociation. The relation,

$$K_D \sqrt[3]{D} = K'_D \sqrt[3]{D'} = K''_D \sqrt[3]{D''} \cdots = \text{Constant},$$

where K_D, K'_D, K''_D represent the dielectric constants of the individual solvents and D, D', D'', the corresponding dilutions at which the value of the degree of dissociation is the same.

From the table[1] on the next page it may be seen, further, that the dielectric constant, and therefore also the dissociating power, is related to various other properties of the solvent.

As the value of the dielectric constant K_D decreases, it is seen that the values of the latent heat of vaporization H_{vap}, of the absolute conductance of heat K_h, and of the critical pressure P_{crit}, also decrease, while the values of the van der Waal constant a and of the molecular volume at the boiling point V_m increase. There is not, however, a strict proportionality.

At this point it should be mentioned that Euler[2] has noticed that the dielectric constants of solutions increase with their ion content. It has, for instance, been shown that the dielectric constant for

[1] *Ztschr. phys. Chem.*, **46**, 172 (1903).
[2] *Ibid.*, **28**, 619 (1899).

water is increased by the addition of a salt to it. It is possible that this fact, even if not alone, plays a part in the deviation of strong electrolytes from the dilution law (see page 125), for naturally the law can only hold as long as the nature of the solvent remains unchanged.

	I	II	III	IV	V	VI
Solvent	K_D	$H_{vap.}$	a	V_m	$P_{crit.}$	K_k
Water	81.7	536.5	5.77	18.9	200	0.154
Methyl alcohol	32.5	267.5	9.53	42.8	79	0.0495
Ethyl alcohol	21.7	205	15.22	62.3	62.8	0.0423
Propyl alcohol	12.3	164	16.32	81.3	50.2	0.0378
Formic acid	57.0	103.7	—	41.1	—	0.0648
Acetic acid	6.5	89.8	17.60	63.8	57.1	0.0472
Ammonia	16	329	4.01	29.2	115	—
Methyl amine	<10.5	—	7.40	—	72	—
Ethyl amine	6.17	—	9.44	—	66	—
i-Propyl amine	5.45	—	13.7	85.6 (normal)	50	—
Sulfur dioxide	14	92.5	6.61	43.9	79	—
Acetone	20.7	125.3	—	77.1	60	—
Methyl-ethyl ketone	17.8	—	11.96	—	—	—
Formic methyl ester	8.87	116.1	11.38	62.7	59.25	—
Formic ethyl ester	8.27	99.3	15.68	84.7	46.83	0.0378
Acetic ethyl ester	5.85	86.7	20.47	106.0	38.00	0.0348
Benzene	2.26	93.5	18.36	96.2	47.9	0.0333
Toluene	2.31	83.6	24.08	118.3	41.6	0.0307
Ether	4.36	84.5	17.44	106.4	35.61	0.0303
Chloroform	4.95	58.5	14.71	84.5	55.0	0.0288
Tetrachlormethane	2.18	46.35	19.20	103.7	45.0	0.0252
Tin tetrachloride	3.2	30.53	26.94	131.1	37.0	—

The Internal Friction and Conductance of Organic Solvents. — With the aid of his comprehensive series of measurements, which have already been mentioned, and also of new determinations of friction coefficients of a large number of organic solvents, Walden[1] has been able to find the relation which exists between the internal friction of a dilute solution of the "normal electrolyte" $N(C_2H_5)_4I$ and the electrical conductance k_∞. He found, moreover, that the

[1] *Ztschr. phys. Chem.*, 55, 207 (1906).

internal friction of dilute solutions and of the solvent are practically identical. Hence in the considerations which are to follow this one value f will be used.

Walden found the following regularities:—

(*a*) Both the internal friction and the conductance are dependent on the nature of the solvent.

(*b*) The smaller the friction, the greater is the value of K_∞, and conversely. From this fact the relationship between the internal friction and the migration velocity of the ions, $N(C_2H_5)_4$ and I′, is evident.

(*c*) The limiting value $K^{25°}_\infty$ is inversely proportional to the corresponding friction coefficients at 25° *t*, according to the equation,

$$K'_\infty : K''_\infty = f''_\infty : f'_\infty,$$

or, in general, according to the equation,

$$K'_\infty \cdot f'_\infty = K''_\infty \cdot f''_\infty = \text{Const.}$$

This constant varies about the value 0.700, between the limits 0.64 and 0.71.

With the use of one and the same electrolyte, it was found that for all of the thirty solvents which were investigated the product of the internal friction and the limiting value of the equivalent conductance was the same, although the individual limiting values varied from about 8 *to* 225.

With the aid of the relation,

$$K^{25°}_\infty \cdot f^{25°}_\infty = 0.700;$$

it is possible to obtain the limiting value of the conductance of the "normal electrolyte" in the solvent under consideration from the value of the internal friction.

Finally, if the temperature coefficients of friction and of conductance be compared, a striking agreement is found, and considering the sources of error involved, it may be said with great probability that *for one and the same solvent the two coefficients are identical.*

From this result it would be expected that the above relation between friction and conductance which holds at 25° would also hold at other temperatures. As a matter of fact it has been found that at 0°

$$K^{0°}_\infty \cdot f^{0°}_\infty = \text{Const.} = 0.700.$$

It therefore follows that

$$K^{25°}_\infty \cdot f^{25°}_\infty = K^{0°}_\infty \cdot f^{0°}_\infty = 0.700.$$

Hence the following general statement may be made:—

With the use of one and the same electrolyte $N(C_2H_5)_4I$ *the product of the internal friction and the limiting value of the equivalent conductance is independent of the nature of the solvent and of the temperature in the case of organic solvents.*

In order to explain these interesting relations, we may assume, as did Kohlrausch in the case of aqueous solutions, that the migrating ion is associated with a large number of molecules of the solvent, and consequently in its forward motion encounters a friction which is identical with the internal friction of the solvent. It is then clear that the temperature coefficient of the limiting value of the conductance and that of the internal friction must become identical.

The Electrical Conductance of Salts in the Fused and Solid States. — The substances which conduct the electric current freely in the state of fusion are chiefly salts and bases, such as silver chloride and caustic soda. Their conductance can be determined by the method used by Poincaré, by using silver electrodes and adding a trace of a silver salt with the same anion as that of the salt being investigated in order to avoid polarization. By this method the measurement can be carried out as in the case of conductors of the first class. The order of magnitude of the equivalent conductance of fused salts is shown by the values, expressed in reciprocal ohms, contained in the following table: —

Salts	Temperature	Equiv. Conductance
KNO_3	350°	44.9
$NaNO_3$	350°	68.0
$AgNO_3$	350°	60.9
KCl	750°	90.6
NaCl	750°	136.3

In order to compare these values with those obtained for salts in dilute aqueous solutions, it will be recalled that the equivalent conductance of a fiftieth normal solution of potassium chloride at 18° is equal to 119.96 reciprocal ohms.

The results thus far obtained in the case of mixtures of fused salts show that their conductance is approximately equal to the sum of the conductances of the constituent salts.

Not only above the melting point, but also below it, many salts conduct the electric current readily. Graetz has investigated the conductance of salts about the melting point, and has found that no considerable sudden change in the conductance occurs as the melting point is passed. On the other hand, the temperature coefficient of

the conductance reaches a maximum value in the vicinity of the melting point.

It is a noteworthy fact that, at lower temperatures (10° to 180°), according to the investigation of Fritsch,[1] the addition of a small quantity of a salt to a large quantity of another salt is, in many cases, accompanied by a great increase in the conductance of the latter salt. This is a striking analogy to the behavior of liquid solutions, justifying the assumption that the one salt exists in solid solution in the other.

The same phenomenon was observed by Nernst[2] in the case of the solid oxides such as magnesium oxide, and it is upon this phenomenon that the Nernst incandescent lamp is based. While the conductance of the pure oxides increases but slowly with the temperature and remains comparatively small, that of a mixture of the oxides increases rapidly, attaining finally an enormous value. For example, values have been observed which were about six times as great as that of the best conducting sulfuric acid solution at 18°.

The fact that glasses also conduct the electric current electrolytically, or, in other words, through the migration of ions, was shown to be very probable by the pretty experiment made by Warburg in the year 1884. He used a piece of glass, one end of which was dipped in sodium amalgam and the other into mercury, as the electrolyte, through which he passed an electric current from the amalgam as anode to the mercury as cathode. After the electricity had passed for some time he found a quantity of sodium equivalent to it in the mercury. Since during the experiment the glass remained clear and constant in weight, it must be concluded that the electricity was conducted almost entirely by means of sodium ions, or, in other words, the migration velocity of the anion, perhaps SiO_3'', is extremely small.[3]

Unipolar Conduction. — It was already observed by Ermann about one hundred years ago that, when the two poles of a galvanic cell are inserted into a well-dried piece of soap, no appreciable continuous current passes through the circuit; and, further, that when one hand is brought into contact with the positive pole and the moistened other hand is pressed upon the soap, an electric shock is received. This latter phenomenon is not observed if, instead of the positive, the negative pole is touched by the hand. From these

[1] *Wied. Ann.*, **60**, 300 (1897).

[2] *Ztschr. Elektrochem.*, **6**, 41 (1899); see also E. Bose, *Drude's Ann.*, **9**, 164 (1904).

[3] Further particulars regarding the conductivity of fused salts may be found in the book of Lorenz, *Die Elektrolyse geschmolzener Salze*, 1905, W. Knapp, Halle, Saxony.

facts, as well as from electroscopic experiments which have been made, it is to be concluded that, whereas the electric current may flow unhindered from the negative electrode into the soap, it cannot do so from the positive pole, but, upon attaching an auxiliary circuit, such as that from hand to hand, it must flow exclusively through this circuit. The soap was called by Ermann a unipolar conductor.

The phenomenon of unipolar conduction was explained by Ohm by assuming that electrolysis takes place in the soap the moment it is connected with the poles of the cell, by which alkali is separated at the negative, and the fatty acid at the positive, electrode. The fatty acid is, however, a nonconductor, and therefore prevents more or less completely the passage of electric current according to the water content of the soap.

Similar observations may be made in the case of the electrolysis of solutions whenever a poor conducting substance is formed at, and adheres to, one of the electrodes. Very recently this has been utilized in a very interesting manner in transforming an alternating into a direct current.

If aluminium be used as an anode in a solution of alkali phosphate, or of alkali salts of the fatty acids, and any other metal as a cathode, a poor conducting aluminium compound is formed on the surface of the aluminium, which prevents the passage of an electric current, even when a potential-difference of 200 volts is applied at the electrodes. When now the two electrodes are connected with the terminals of a circuit carrying an alternating current, only the current in one direction is allowed to pass. The alternating is thus transformed into direct current. This application of unipolar conduction will, however, scarcely become of practical importance.

It appears doubtful that, in the case of the above aluminium cell, the whole action can be explained by the fact that a relatively thick layer of great resistance is formed at the anode. It is more probable that a thin dielectrum of slight conductance is formed at the electrode, thus forming a powerful acting condenser in the circuit.

Technical Importance of Electrical Conductivity. — A knowledge of the conductivity of various solutions (and of fused salts) under the most varied conditions is essential to the rational management of an electrolytic industry, for it should always be the aim to work with the best possible conducting solutions. Thus, if other circumstances do not prevent it, a solution of potassium chloride is always to be preferred to a solution of sodium chloride of the same molar concentration. Furthermore, it is always preferable to carry out an electrolytic process at a high temperature, if the cost of heating

does not exceed the saving in electrical energy due to the increase in conductivity. Since very often the concentration can be chosen at will inside of wide limits without injury to the process, that concentration should, in such cases, be chosen which has the greatest *specific conductance*. In this connection it should be remembered that, in the case of electrolytes which are very soluble in water, the specific conductance, or conductivity, in contrast with the equivalent conductance, at first increases and then decreases with increasing concentration. This is shown by the results for sulfuric acid at 18°, given in the following table: —

Percentage Concentration	Specific Conductance
20	0.6527
25	0.7171
30	0.7388
35	0.7243
40	0.6800
70	0.2157

Hence, whenever sulfuric acid is used as an electrolyte, as, for example, in the case of the electrolytic regeneration of chromic acid where only about 100 grams of chromic oxide as an acid salt in sulfuric acid is contained in one liter of solution, the conductance is increased by the addition of an electrolyte, which is without injury to the process. In the above chromic acid process sulfuric acid serves as such an electrolyte, enough being added to increase the specific conductance of the mixed electrolytes to its maximum value. Very often it is necessary for the electro-chemist to make his own measurements, in order to find the best proportions of electrolytes to use in a given case.

The investigation of the cause of benzene conflagrations[1] has shown that the practical application of electrical conductance to poor conductors may give rise to great fire danger. The electrostatic charges generated by friction are prevented from being conducted away rapidly enough by the poor conductance of the pure benzene. This leads to the formation of electric sparks, which, of course, may easily cause explosions. An addition to the benzene of a small quantity of a magnesium salt of a fatty acid increases the conductance sufficiently to prevent the formation of the sparks.

The conflagrations which suddenly break out during work with other poor conducting organic liquids, such as acetone, ether, etc., may be explained in the same manner.

[1] Just, *Ztschr. Elektrochem.*, 10, 202 (1904).

CHAPTER VI

ELECTRICAL ENDOSMOSE. MIGRATION OF SUSPENDED PARTICLES AND OF COLLOIDS. ELECTRO-STENOLYSIS

As early as the year 1807 Reuss observed that, during the electrolysis of water contained in a vessel which was divided into an anode and a cathode section by a capillary, or a system of capillaries such as a porous diaphragm, the water was carried by the current from the former to the latter section. In the case of the better conducting solutions, this phenomenon, or *electrical endosmose*, is not very pronounced.

Later on, Quincke and G. Wiedemann carried out further experiments in this direction. The following statement was found by Wiedemann to express the laws of electrical endosmose for a given liquid: —

The quantity of a given liquid carried through a porous diaphragm in a definite time varies directly with the current strength and is independent of the area or thickness of the diaphragm.

In 1809 Reuss observed that suspended particles, such as clay, etc., are migrated under the influence of a fall in potential. When suspended in water, they are migrated toward the anode. Recently such migrations in the case of the so-called colloidal solutions have been closely studied. This has led to the recognition of two classes of colloids, namely, positive and negative colloids. The positive colloids, such as gold, platinum, cadmium, antimony, arsenic sulfide, molybdinum blue, indigo, etc., migrate toward the anode, while the negative colloids, such as ferric hydroxide, aluminium hydroxide, chromium hydroxide, hemoglobin, methyl violet, etc., migrate toward the cathode. The behavior of suspensions of nickel, zinc, and copper oxide is more complicated. In these cases, the addition of small quantities of foreign material, such as traces of alkali or of acid, changes the direction of migration.

It is interesting to note that a difference between positive and negative colloids also appears in the case of their precipitation. The positive colloids are more easily precipitated by means of NaOH, while the negative are more easily precipitated by HCl. The former

are also precipitated by the β-radium rays, which contain negative electrons, while the latter are not. Finally, if the two kinds of colloids are brought together, they precipitate each other. It is a peculiar fact, however, that this precipitation does not take place if the two colloids are not brought together in certain proportions.[1]

It is evident from the above experiments that the electric current exerts a force in a certain direction, not only upon ions, but also upon other movable bodies of matter. This may, in all cases, be explained by the assumption of the presence of an electrical charge upon the portion of matter in question. The probability that this assumption is correct is greatly increased by the deductions of Helmholtz. He reasoned that at the surfaces of contact of two dissimilar media, for instance the contact surface of water and glass, an electrical charge or double layer must form. The existence of such a double layer seems comprehensible from the results of experiments on the formation of contact or frictional electricity. If now a potential-fall is produced in a liquid by the passage of an electric current through it, then the positive part of the double layer is attracted by the negative, and the negative part by the positive, pole. Thereby a displacement of the two layers takes place, resulting, when the force of the current is sufficiently great, in the migration phenomenon noted above. The movable liquid layer, according as it is charged positively or negatively, migrates toward the cathode or anode, respectively, and by means of friction carries with it the neighboring liquid or in case the migration takes place in capillaries, the entire liquid. The disrupted double-layer gradually becomes neutral by conduction, forming a new double-layer, and the process goes on again. By means of a suitable pressure, moreover, as much liquid may be forced back through the center of the tube as is brought up by the electric current along the walls of the tube, thus establishing a stationary state. Conversely, if by means of a powerful pressure the liquid be forced through a capillary tube so that the charged liquid forming a part of the double layer is forced along the wall of the tube together with the current of liquid in the middle of the tube, an electric current is produced. The arrangement is entirely analogous to the ordinary electric machine, with only this difference, that whereas in the former case a liquid rubs past a solid, in the electric machine a solid rubs past a solid.

This explanation is naturally directly applicable to the migration of suspended particles. These particles take the place of the glass wall and, being movable, migrate, in the opposite direction from the

[1] Biltz, *Ber.*, **37**, 1095 (1904).

water, to the anode.[1] The question arises as to what other properties may be connected with this phenomenon. If now another liquid be substituted for water, a change will be observed. When turpentine, for example, is substituted, it migrates to the anode, while the suspended particles migrate to the cathode. Coehn gives the following answer to the above question,[2] which he has confirmed by many experiments: *If two substances are brought into contact with each other, that one possessing the higher dielectric constant will become positively charged.* It has already been stated that water possesses a very high dielectric constant. This fact then furnishes a ready explanation for the migration of water, in most cases, to the cathode.

The technical application of the phenomenon of electrical endosmose has recently been undertaken.[3] If a vessel, the opposite sides of which are formed of perforated pieces of metal serving as electrodes, be filled with a quantity of wet turf, and an electric current be passed through it, water bubbles out of the perforations in the side forming the cathode. This is a striking lecture experiment. The turf itself which becomes dried acts as a diaphragm, while the water is carried to the cathode, where it flows off. In a similar manner it was endeavored to extract the sap from sugar beets, and to accumulate it about the cathode, preparatory to the crystallization of the sugar. It is not at present known, however, whether or not the extensive experiments have shown the process to be of commercial value.

In the electrical tanning process, electrical endosmose appears also to play a leading rôle, by forcing the tanning liquids quickly into the pores of the hides.

An observation of Braun is closely related to electrical endosmose. He observed that when a salt solution separated into two portions by capillaries is electrolyzed, a deposition of metal takes place in the capillaries. This phenomenon is called *electrostenolysis.* Capillaries, most suitable for demonstration purposes, may be prepared by dipping the hot closed end of a glass tube into cold water. This end is then pierced by numberless fine cracks. If now a solution and one electrode be placed in this tube, and the tube be placed in a beaker also containing solution and the other electrode, the desired apparatus is obtained.

Electro-stenolysis has also been explained by Coehn.[4] It has

[1] Another theory has been advanced by Billitzer, *Ztschr. phys. Chem.*, **45**, 307 (1905).

[2] *Wied. Ann.*, **64**, 217 (1898).

[3] German Patents 124509, 124510, 128085.

[4] *Ztschr. Elektrochem.*, **4**, 501 (1898); *Ztschr. phys. Chem.*, **25**, 651 (1898).

already been noted that with a sufficiently great potential-fall, a displacement of the positive water layer takes place, leaving the glass wall of the capillary negatively charged. If now positively charged metal ions are present in solution, they will be attracted to the wall of the capillary, and there discharged and deposited. To be sure, this deposition will be very slight since very large electrical charges are present on the ions. The metal layer deposited cannot in general be increased by taking part in the conduction, because one end then becomes an anode and loses as much metal as the other end gains as cathode. Under these circumstances, only a displacement of the layer in the direction of the cathode can take place. In those cases, however, in which the weight of the layer can increase by taking part in the conduction of electricity, the trace of deposited metal increases and finally becomes visible.

Such cases are the following:—

1. When the deposited metal is not oxidized at the anode, as, for example, the platinum salts.

2. When an insoluble compound is formed at the anode, especially the peroxides.

3. When, in the case of salts in the lower state of oxidation, the negative ion can react on the solution with the formation of a higher oxidized salt as in the case of a cuprous chloride solution. In this case the chlorine liberated oxidizes the salt to cupric chloride.

As a specially interesting result of the experiments substantiating these statements, it may be mentioned that solutions of cobalt salts, which are weakly acid through hydrolysis, show stenolysis regularly, while in the case of nickel salts no deposition of metal is visible. It was concluded from this fact, that of the two, only the cobalt salts form peroxides by electrolysis. Utilizing this fact, not only a simple and certain qualitative test for cobalt in nickel solutions, but also a quantitative, although somewhat tedious, separation of the two metals is possible.[1]

[1] *Ztschr. anorg. Chem.*, **33**, 9 (1903).

CHAPTER VII

ELECTROMOTIVE FORCE

HAVING dealt in the previous chapters especially with the one factor of electrical energy, the quantity of electricity, the other factor, the electromotive force, will now be considered.

The Determination of Electromotive Force. — As already indicated in the introduction, the electromotive force of a cell may be determined by means of a delicate galvanometer through an application of Ohm's law,

$$C = \frac{E}{R_{in} + R_{ex}},$$

when R_{ex} is made so great that R_{in} is inconsiderable in comparison with it. In this case, the deflections of the needle of the galvanometer caused by two different cells successively introduced into the same circuit are to each other as the respective electromotive forces of the cells. If one of the two cells be a normal cell, the electromotive force of the other cell is thus easily obtained directly in volts. If the internal resistance has not been made negligible compared with the external, the electromotive force may still be determined by reading the galvanometer deflections caused by the two cells, both connected in the same circuit, first in series and secondly in opposition to each other. In this case we have the equation,

$$\frac{C_1}{C_2} = \frac{E_x + E_n}{E_x - E_n};$$

or

$$E_x = E_n \frac{C_1 + C_2}{C_1 - C_2};$$

in which C_1 and C_2 are the currents found in the two cases and E_x and E_n are the electromotive forces, respectively, of the unknown and of the normal cell.

In more general use than the above method is that devised by Poggendorf and known as the *compensation method*. By this method, the unknown electromotive force is exactly compensated by a known

electromotive force. A diagram of a convenient form of apparatus for this method is shown in Figure 33.[1]

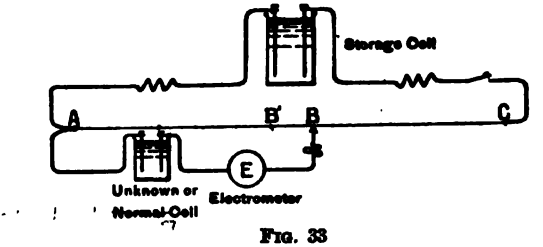


FIG. 33

In the above figure, the line AC represents the meter wire of a Wheatstone bridge or of a drum, usually of about ten ohms resistance. The other parts are named in the figure. When the storage cell is in place, a current flows through the wire AC and there is a definite and uniform fall in potential between the points A and C. In order to obtain the value of this potential-fall, a carefully tested normal cell and an electrometer, galvanometer, or any other instrument which shows when no current is flowing in a circuit are connected in an auxiliary circuit as shown in the diagram, and the sliding contact B is moved until the electrometer indicates that no current is flowing in this circuit. The potential-fall between the points A and B is, then, equal to the known electromotive force of the normal cell. Since the fall in potential is uniform along the wire, the fall per millimeter of the wire may then be calculated.

The unknown electromotive force of any other cell may now be determined by substituting it for the normal cell and again moving the sliding contact until no current flows in the circuit. If the new position of the sliding contact is B', then the unknown electromotive force is equal to the known potential-fall from the point A to the point B'.

When the electromotive force of a cell is to be measured, that which it possesses on an open circuit is, in general, the value desired, for the value which would be obtained while the cell is in action would be indefinite because of the change in the state of the electrodes or of the electrolyte which takes place. In the case of electrometric, and especially in the case of galvanometric, measurements, the conditions under which no current flows in the

[1] For a more detailed description, see Ostwald-Luther, *Physiko-chemische Messungen*, page 367. For a more sensitive potentiometer based on the same principles, see Jäger, *Die Normalelemente* (Wihl. Knapp, Halle, Saxony, 1902).

circuit do not strictly prevail even when according to the electrometer, or other instrument, they should be fulfilled. This is due to the fact that every instrument consumes, at the expense of the source being measured, a certain quantity of electricity for its operation. It is necessary, therefore, to ascertain whether or not this quantity of electricity is greater than allowable, or in other words, whether or not the state of equilibrium actually measured is appreciably different from that which it is desired to measure. As a matter of fact, in the case of measurements made on gas and similar cells, a considerable error is frequently introduced because of failure to pay sufficient attention to the sensitiveness of the galvanometer or to the capacity of the electrometer.

The following normal cells are those most generally used:[1]—

1. The so-called *Helmholtz calomel cell*, which consists of

$$Zn - ZnCl_2 \text{ solution (sp. gr. 1.409 at 15°)} - HgCl - Hg.$$

This cell, when made in the prescribed manner, possesses an electromotive force of one volt at about 15° t. The change of the electromotive force is very small, being equal to $+ 0.00007$ for a rise of one degree.

2. *The Clark cell*, which consists of

$$Zn - ZnSO_4 \text{ paste} - Hg_2SO_4 \text{ paste} - Hg.$$

When made according to the specifications of the "Physikalisch-Technischen Reichsanstalt," it has an electromotive force of

$$1.4328 - 0.00119\,(t - 15) - 0.00007\,(t - 15)^2 \text{ volts},$$

where t is its temperature.

(3) *The Weston or cadmium cell*, which consists of

$$Cd \text{ (better a 10 to 15\% amalgam)} - CdSO_4 \text{ paste} - Hg_2SO_4 \text{ paste} - Hg.$$

This cell, when made in the prescribed manner, has an electromotive force of

$$1.0186 - 0.000038\,(t - 20) \text{ volts},$$

and is preferable to the Clark cell, because its temperature coefficient is nearly zero.

For exact measurements it is recommended that normal cells be obtained from the "Technischen Reichsanstalt." The electro-

[1] For further particulars, see Ostwald-Luther, *Physiko-chemische Messungen*, page 361; Jäger, *Ztschr. Elektrochem.*, 8, 485; and Jäger, *Die Normalelemente* (Wihl. Knapp, Halle, Saxony, 1902); Hulett, *Ztschr. phys. Chem.*, 49, 483 (1904).

motive force of these cells is obtained from measurements of resistance and current.

Reversible and Irreversible Cells. — Any arrangement which, as a result of a chemical reaction or of such physical processes as diffusion, etc., is capable of producing electrical energy is called a galvanic cell; whether the reaction takes place between a liquid and a solid or between two liquids does not come into consideration. All cells, or, as they are also called, elements, may be divided into two classes, namely, into those which are *reversible* and those which are *irreversible*. To the first class, for example, belongs the Daniell cell, which consists of

$$Zn - ZnSO_4 \text{ solution} - CuSO_4 \text{ solution} - Cu.$$

The meaning of the term *reversible cell* may be made clearer by the following consideration: Let us consider, for example, a Daniell cell, the electromotive force of which is exactly compensated by another, oppositely directed, electromotive force. If the latter be now slightly diminished, the cell at once becomes active, zinc goes into solution, and copper separates out. On the other hand, if the compensating electromotive force be, instead, slightly increased, thus becoming slightly greater than that of the Daniell cell, copper dissolves, and the zinc deposits out of solution. Hence, if the condition of the cell is changed by a process like the former, this change may be exactly compensated and the original condition of the cell restored by a process like the latter, *i.e.* the cell is reversible. Of a reversible cell it is theoretically true that the maximum electrical energy which can be obtained through its action at constant temperature exactly suffices to bring it back to its former condition. This statement may also be taken as a definition of a reversible cell.

As an example of an irreversible cell, that one discovered by Volta which consists of

$$\text{Zinc} - \text{dilute sulfuric acid} - \text{silver}$$

may be given. When this cell is in operation, zinc dissolves, and hydrogen separates at the silver electrode and is lost. From this fact alone it is evident that the original condition cannot be restored by simply reversing the current. On the contrary, in this case silver goes into the solution, and hydrogen separates at the zinc electrode.

It is characteristic of reversible cells that, when the current is not too great, the electromotive force which they possess immediately after being set into operation remains nearly constant as long as

the material necessary for the chemical reaction is present. On the other hand, the initial high electromotive force of an irreversible cell falls considerably, and reaches a nearly constant minimum only after some time. Hence the terms, *non-polarizable* and *polarizable*, which are often applied to these two classes of cells. More definite information relating to these phenomena will be given later, in the chapter on polarization. It may, however, be stated here that a metal which is not too positive, dipping into a solution which contains a sufficient number of its own ions (preferably a saturated solution in contact with some of the solid salt), forms, for ordinary current densities,[1] a non-polarizable electrode. In the case of the Daniell cell both electrodes, and consequently the whole cell, is non-polarizable.

Since at the present state of science the actions which take place in reversible cells may easily be comprehended, and even quantitatively followed, they may now be considered to advantage.

Relation between Chemical and Electrical Energy II. — The question now arises: How may the quantity of electrical energy which a cell is capable of producing be calculated from the chemical energy expended, — or, more strictly speaking, — from the heat effects of the reactions taking place in the cell, since the latter still constitute our measure of the chemical energy? It has already been mentioned in the introduction that the assumption originally made by Helmholtz and William Thomson, that the quantities of heat involved are completely transformed into electrical energy, is untenable. It is only in certain rare cases that this simple relation exists. About thirty years ago Gibbs, Braun, and Helmholtz succeeded, by calculation, in fixing the real relations.

The first law of energetics may be stated as follows: —

Energy can neither be created nor destroyed, and consequently the total quantity of energy is a constant.

This law says nothing about the possibility of transforming one energy form into another, and, indeed, from it alone it appears as if it would be possible to transform heat at constant temperature into work. If this were true, it would no longer be necessary to use expensive coal to furnish power to run our railroad trains, for the inexhaustible heat energy of the surroundings could be used

[1] Current density may be defined to be the current per square centimeter of electrode surface. While the total current is the same at both anode and cathode, the current density at the two electrodes varies according to the respective sizes of the electrodes. It is therefore usual to distinguish an anode and a cathode current density.

instead. As a matter of fact, it has not been found possible to obtain such a form of perpetual motion, called perpetual motion of the second kind. This experience has resulted in the formulation of the second law of energetics, which excludes the unlimited transformability of the forms of energy. It was expressed by Clausius as follows: —

Heat cannot pass of itself from a lower to a higher temperature.

The following more general statement of the law by Nernst is, however, to be preferred: —

"Every process which takes place of itself in any system, or, in other words, without receiving energy in any form from the surroundings, is capable of furnishing a definite quantity of work."

Conversely, such a process can be made to take place in the opposite direction only by the expenditure of work upon it. If no spontaneous processes existed, then no work of any kind could be performed. For example, at constant temperature, and excluding other changes in state, a transformation of heat into work is impossible.

It should be borne in mind that these two laws of energetics express the conclusions of experience and not the deductions from theories.

The maximum external work which a spontaneous process is capable of furnishing is of great interest, since this work is an important characteristic of the process. It is not worth the trouble to investigate values other than the maximum value, because they are indefinite and may vary even to zero.

From a closer consideration, it is evident that the maximum quantity of work is obtained from a process when it is made to take place reversibly, or, in other words, in such a manner that, theoretically speaking, at every instant equilibrium exists in the process.

A process may be carried out isothermally and reversibly in several ways. The question then arises as to whether the values of the maximum work obtained in these different ways are identical? Now they must be identical, for otherwise perpetual motion of the second kind would result, and this, according to the second law of energetics, is an impossibility. Therefore if the value of the maximum work of a process when carried out in one way, is known, its value when the process is carried out in any other way is also known. If, for example, the maximum osmotic work which a process is capable of producing is known, then the maximum quantity of electrical energy which may be obtained from it is also known. When, further, the quantity of substance, and so the quantity of electricity,

involved is known, the electromotive force may at once be calculated with the aid of Faraday's law as follows: —

Electromotive force × Quantity of electricity = Electrical energy.

Hence $$\text{Electromotive force} = \frac{\text{Electrical energy}}{\text{Quantity of electricity}}.$$

From the above discussion, it is evident how important it is, especially for the calculation of electromotive forces, to know the maximum external work obtainable from an isothermal process. Such knowledge will be applied later on in the book. The second law of energetics may also be stated in the following form: —

The sum of the quantities of work involved in the different parts of an isothermal, reversible, cyclical process is equal to zero.

It is also of great importance in electro-chemistry to know the maximum quantity of work obtainable when a given quantity of heat is lowered from one temperature to another; for this, too, is a spontaneous process. In order to find this quantity of work, it is necessary to devise a process by means of which heat may be transferred reversibly from one temperature to another which is lower. Such a process is easily found. As the machine or carrier of heat from the one temperature to the other a perfect gas may be used. In this case the calculation is especially simple. It is only necessary to be able to determine the quantity of work obtainable when a gas of a volume v and pressure p changes isothermally to a volume v' and pressure p'. This quantity of work is the same as that obtainable when an "ideal" solution of a volume V and osmotic pressure P changes isothermally to the values V' and P' respectively. As frequent use of osmotic work will be made, the following derivation is of twofold interest.

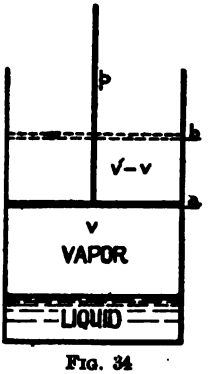


FIG. 34

If in the apparatus shown in Figure 34 one mol of a saturated vapor (in contact with its liquid) of volume v and pressure p be allowed to expand against the constant pressure p until the volume v' is reached, the maximum work obtainable is easily calculated. If it be imagined that the increase in volume $(v' - v)$ is divided into infinitely small parts designated by dv, then the work obtainable during each successive expansion of dv is equal to pdv, and the total work,

$$W = p\int_{v}^{v'} dv.$$

Expressed in words, the total work is equal to p times the sum of these infinitely small volumes dv from the value v to that of v'. Consequently

$$W = p(v' - v).$$

Attention is here called to page 4 of the introduction, where it is shown that the product pv, and therefore $p(v' - v)$ or pv'', represents a quantity of work [and also to Figure 35, which is a graphical representation of the relation of p, $v' - v$, and W].

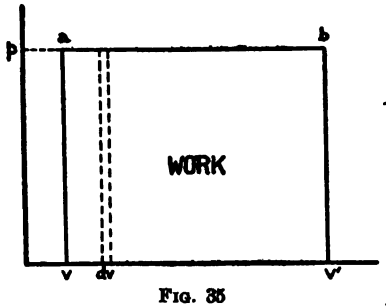


FIG. 35

In the case now to be considered, the relations are not quite so simple, since the pressure, instead of remaining constant as in the above case, continually changes with the volume until it reaches the value p'. We have not then merely to add together the values of dv; the sum of the endless number of infinitely small quantities of work pdv must be found, where the value of p is no longer a constant but a function of v, or in other words, where the value of p depends upon and varies with the value of v. The quantity of work involved during the change in volume and pressure of the perfect gas is given by the equation,

$$W = \int_v^{v'} p dv.$$

The values of p and v are dependent upon each other in a definite and known manner. For one mol of a gas, the following equation holds (see page 53):—

$$pv = RT;$$

or

$$p = \frac{RT}{v}.$$

By substituting this value of p in the above equation and placing the constants before the sign of summation (the integral sign), the following equation is obtained:—

$$W = RT \int_v^{v'} \frac{dv}{v}.$$

There is here only one variable, and the integral is determinable. From integral calculus it is known that

$$\int_v^{v'} \frac{dv}{v} = \ln \frac{v'}{v}, \text{ or } = \frac{1}{0.4343} \log \frac{v'}{v},$$

where ln signifies the natural and log the ordinary logarithm; consequently

$$W = RT \ln \frac{v'}{v} = \frac{RT}{0.4343} \log \frac{v'}{v}$$

Since, according to the gas law of constant pressure-volume product (Boyle-Mariotte),

$$\frac{v'}{v} = \frac{p}{p'},$$

the above equation may also be written as follows:—

$$W = RT \ln \frac{p}{p'} = \frac{RT}{0.4343} \log \frac{p}{p'}.$$

It is evident, from the above equation, that the available work is proportional to the absolute temperature of the gas, and further, that it does not depend upon the absolute values of the pressure or volume, but upon the relation between the respective values of each. Accordingly, the quantity of available work is the same whether the gas passes from a pressure of ten to a pressure of one atmosphere, or from a pressure of one to a pressure of one tenth of an atmosphere.

It may be recalled that when it is desired to express the work in

mean gram-calories, the value of $R = 1.985$,
gram-centimeters, the value of $R = 84800$ (approx.), and in
joules, the value of $R = 8.32$.

[The relation between the pressure and volume changes and the maximum quantity of work obtainable during an isothermal expansion of a gas is shown graphically in Figure 36. The line *ab* is the pressure-volume curve and the area *abvv'* represents the work done by the gas in expanding from the volume v to v' at constant temperature. In the above mathematical derivation of the equation representing the work, therefore, this area has been found by obtaining the sum of the infinitely small areas pdv of which it is composed.]

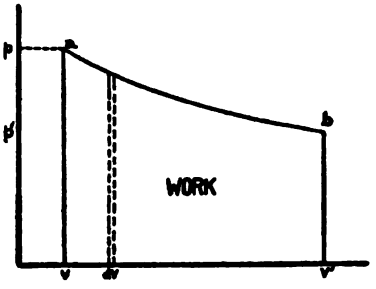


FIG. 36

If one mol of a gas expands so that its pressure decreases to one hundredth of its original value, or, what is the same, its volume increases a hundred fold, the maximum quantity of work obtainable from the process at 17° t or 290° T is given by the following equations: —

$$W = \frac{1.985 \times 290}{0.4343} \log \frac{100}{1}, \text{ or } 2651 \text{ gram-calories,}$$

or $$W = \frac{84800 \times 290}{0.4343} \log \frac{100}{1}, \text{ or } 113250 \times 10^3 \text{ gram-centimeters.}$$

If, instead of one mol, n mols of gas had been taken, the quantity of work obtainable would have been n times as great.

It may be well to remark that this work which is obtained during the isothermal expansion of a gas is not taken from the internal energy of the gas itself, but from the heat energy of the surroundings. The gas serves only as a medium for the transformation of heat into work.

It is now possible for us to consider the process for the reversible transference of heat from one temperature to another, and to calculate the quantities of work involved in the different parts of the process.

Part 1. One mol of the gas is compressed reversibly at the temperature T from a volume v' to the volume v. The work done upon the gas is given by the equation

$$W_1 = RT \ln \frac{v'}{v}.$$

This quantity of work is converted into heat, which is absorbed by the surroundings. Moreover, the quantity of heat thus set free is, according to the first law of energetics, equivalent to the work done, or

$$Q_1 = RT \ln \frac{v'}{v}.$$

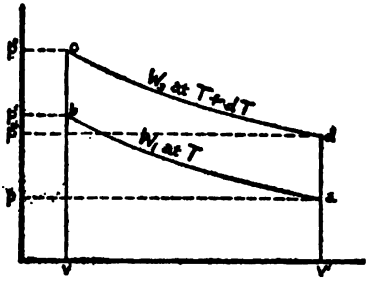


Fig. 37

[This quantity of heat and of work is represented in Figure 37 by the area $abv'v$.]

Part 2. The gas is now brought into surroundings of a temperature $T + dT$. The quantity of heat thereby absorbed by the gas is negligibly small as compared with Q, and, moreover, the same quantity is given off to the sur-

roundings in a later part of the process. Since the volume v of the gas remains constant during the change in temperature, no external work is done. [This change is represented by the line bc in Figure 37.]

PART 3. At the new temperature, the gas is expanded reversibly from volume v to volume v'. The work done by the gas is, then,

$$W_2 = R(T+dT)\ln\frac{v'}{v} = RT\ln\frac{v'}{v} + RdT\ln\frac{v'}{v}.$$

A quantity of heat equivalent to this work is absorbed from the surroundings,—

$$Q_2 = RT\ln\frac{v'}{v} + RdT\ln\frac{v'}{v}.$$

[W_2 and Q_2 are represented by the area $cdv'v$.]

PART 4. Finally, the gas is brought into surroundings of a temperature T. After the same negligible quantity of heat as was absorbed in part 2 has been given out to the surroundings, the process has passed along the line da to a, and the gas is in its original condition. The process is now complete.

As a final result of the whole process, it is evident that the quantity of work W obtained is as follows: —

$$W = W_2 - W_1 = RdT\ln\frac{v'}{v} = Q_1\frac{dT}{T}.$$

[Referring to the figure, W is seen to be equal to the area $abcd$.] An equivalent quantity of heat has therefore been transformed into work, but at the same time the quantity of heat

$$RT\ln\frac{v'}{v}$$

has disappeared at the temperature $T+dT$, and been recovered at the temperature T. Here there are two different kinds of heat transformations taking place simultaneously. A definite quantity of heat Q' can only be transformed into work by a reversible-cyclical process operating between the temperatures $T+dT$ and T when another definite quantity of heat Q passes from the higher to the lower of these two temperatures. The following equation gives the relation which exists between these two quantities of heat: —

$$Q' = Q\frac{dT}{T}.$$

The result of the above deduction is of general application.

Whenever a quantity of heat is transferred from a higher to a lower temperature, and no other change in state takes place, only a fraction of it can in any case be transformed into work. The relation between this fraction and the rest of the heat when the maximum quantity of work is obtained is given by the above equation.

Let us apply these considerations to the reversible galvanic elements. If the heat evolved by the reactions taking place within such an element, having no internal resistance, be entirely changed into electrical energy while the element is immersed in a calorimeter, no heating effect would be observed. The reason is that just as much energy as was produced would be consumed as electrical energy (capable of transformation into work) in the external circuit. As a matter of fact this simple relation very seldom exists, and therefore a generation of heat in the calorimeter can usually be observed.

Imagine a reversible cell of electromotive force E at the temperature T, and suppose the quantity of electricity, 96,540 coulombs, or ε, be passed through it, then the maximum electrical energy which may be produced is $E\varepsilon$. Let Q be the sum of the heats of the corresponding reactions. The action of the cell is attended by absorption of heat, the heat absorbed being $E\varepsilon - Q$, according to the first law of energy. Suppose the temperature increased by dT and the amount of electricity ε again sent through the cell, but in the opposite direction, and under the new electromotive force, $E + dE$; the amount of work thus consumed will be $\varepsilon(E + dE)$. The corresponding sum of the heat of reaction in this reversed process has changed but little, and, neglecting this change, is $Q + dQ$. The heat generated in the cell is in this case equal to the difference between the electrical energy used and the heat taken up in the chemical processes, and is thus equal to $E\varepsilon + \varepsilon dE - (Q + dQ)$. If the element be brought again to the temperature T, it is once more in its original condition.

As the end result of the process, the work εdE has been performed, and accordingly the equivalent amount of heat εdE produced. At the temperature T the heat $E\varepsilon - Q$ has been lost, but at $T + dT$ the heat $E\varepsilon + \varepsilon dE - (Q + dQ)$ has been obtained, which with slight error may be simplified to $\varepsilon E + \varepsilon dE - Q$. As εdE is derived from the work done, the amount of heat $E\varepsilon - Q$ has been raised from the temperature T to $T + dT$. Conversely, in order to change the quantity of heat εdE into work, the amount of heat $\varepsilon E - Q$ must fall from the temperature $T + dT$ to T, consequently the following expressions are correct in accordance with page 171:—

$$\underline{Q}d\mathrm{E} = (\mathrm{E}\underline{Q} - Q)\frac{dT}{T}; \tag{1}$$

$$\mathrm{E}\underline{Q} - Q = \underline{Q}T\frac{d\mathrm{E}}{dT}; \tag{2}$$

$$\mathrm{E} = \frac{Q}{\underline{Q}} + T\frac{d\mathrm{E}}{dT}. \tag{3}$$

Since we can calculate Q from thermochemical data, or can determine it directly, we are able, with the help of the experimentally determined temperature coefficient of the electromotive force, to calculate the maximum electrical energy obtainable, or the electromotive force of the cell. In the thermochemical data the numbers always apply to a gram equivalent or gram-molecule, the heat generated being considered positive.

If the temperature coefficient is positive, *i.e.* if the electromotive force increases with rise of temperature, it follows from equation (2) that $\mathrm{E}\underline{Q}$ is greater than Q: the cell in activity tends to become cooler, and so takes heat from the surroundings. If, on the other hand, the temperature coefficient is negative, $\mathrm{E}\underline{Q}$ is less than Q, and the cell becomes warmer. If finally the temperature coefficient is zero, the heat of reaction is simply and completely transformed into electrical energy, and the cell itself exhibits no thermal change. This latter condition is nearly realized in the Daniell cell.

It is necessary to emphasize this fact that the heat of the chemical reactions is not a strict measure of the available electrical energy of a reversible element, although experience has shown that in many cases it enables us to estimate it approximately, since $\frac{d\mathrm{E}}{dT}$ is very often negligible as compared with Q, and therefore may be omitted from equation (3).

The above formula of Helmholtz has been qualitatively proven by Czapski and Gockel, and quantitatively by Jahn and others. Several apparent contradictions, as later shown by Nernst, arose from erroneously assumed values for the heat of formation of mercury compounds.

For illustration, the values found by Jahn[1] and Bugarszky[2] are given in the table on the next page.

In the table, E denotes the electromotive force at 0°, $\frac{d\mathrm{E}}{dT}$ the

[1] *Wied. Ann.*, **50**, 189 (1893).
[2] *Ztschr. anorg. Chem.*, **14**, 145 (1897).

change in electromotive force per degree, 2 FQ the electrical energy given out by the cell when two equivalents of the substances have reacted, and H_r the heat of reaction for the same quantities of the reacting substances, expressed in calories. In the last two columns are given the values of the heat effect in the cell, *i.e.* those calculated from $\frac{dF}{dT}$ and from the expression, $Q - 2\,FQ$, respectively.

Cell	F, at 0°	$\frac{dF}{dT}$	2 FQ	H_r	Heat Effect in Cell	
					Calc.	$Q - 2\,FQ$
$Cu-CuSO_4 + 100\,H_2O$ / $Zn-ZnSO_4 + 100\,H_2O$	1.0962	+0.000034	50526	50110	− 428	− 416
$Ag-AgCl$ / $Zn-ZnCl_2 + 100\,H_2O$	1.015	−0.000402	46907	52046	+ 5082	+ 5139
$Ag-AgBr$ / $Zn-ZnBr_2 + 25\,H_2O$	0.828	−0.000105	38276	39764	+ 1326	+ 1488
$Hg-HgCl + KCl, 0.01C_n$ / $1\,C_n, KNO_3$ / $Hg-Hg_2O + KOH, 0.01\,C_n$	0.1483 t=18.5°	+0.000837	7566	−3280	− 11276	− 10846

As is evident, the agreement between the heat value of the cell as observed in the calorimeter and that calculated from the difference between the electrical energy produced by the current and the corresponding heat of reaction is satisfactory in each case. The last set of measurements is particularly interesting, since the chemical process which spontaneously gives rise to the electric current is endothermic and the cell when in operation absorbs heat from the surroundings. It furnishes a striking proof of the incorrectness of the assumption that the heat of reaction is a measure of the work obtainable from a cell.

The above equations have also been found to hold for cells of fused electrolytes at high temperature.

It may be advisable to add that electrical energy may be measured by inserting the cell in a circuit, the resistance of which is so great that internal resistance of the cell is negligible in comparison. The electrical energy being allowed to change into heat, the amount of the latter generated in the unit of time is C^2R, according to Joule's law (page 18), where R represents the resistance of the circuit, and C the current-strength. Knowing the resistance R, and having measured the current-strength, the quantity of electrical energy produced per unit time may be calculated. From this the quantity of energy produced when 96,540 coulombs, or twice

that number, pass through the circuit may be easily determined, the choice between these numbers depending upon whether one or two gram equivalents of the substances take part in the chemical reaction. As the internal resistance of the cell itself is negligible compared to the external, the electrical heat effect produced within the cell is insignificant, and may be left out of consideration. The heat generated in the cell, and measured in a calorimeter as previously described, has nothing to do with the electrical heat effect, c^2R, which is the heat generated by the electric current and hence a measure of the electrical energy furnished by the cell. It is, instead, equal to the difference between the heat of the reactions which take place in the cell and the electrical heat effect just mentioned.

The equation previously derived enables us to determine the electromotive force of a cell from a knowledge of its temperature coefficient and of the heat of reaction. The electromotive force of reversible cells may be determined in another manner, as already indicated on page 166. Before proceeding with the calculation, a clear idea of the concept, *electrolytic solution tension*, which was introduced by Nernst, is necessary.[1] We will, however, follow Ostwald's nomenclature and call it *electrolytic solution pressure*.

Electrolytic Solution Pressure. — The expression "vapor pressure of a substance" is one commonly understood. It signifies the tendency of a substance to enter the gaseous state. If, for example, we allow water at a certain temperature to evaporate in a long cylindrical vessel, as shown in Figure 38, in which there is a movable air-tight piston, and if a pressure p' is exerted upon the piston less than the vapor pressure of the water, the piston is moved upwards and more water evaporates. Hence a condition of equilibrium is only established when a certain definite pressure equal to p is exerted upon the piston from without. The latter will then remain stationary in whatever position it be placed as soon as equilibrium between water and vapor obtains. If the pressure on the piston be slightly increased, the piston will fall and all of the vapor will condense to water; if, on the other hand, it be slightly diminished, the piston will rise and all of the water will vaporize. The pressure downward on the piston at equilibrium represents the vapor pressure of water at the temperature of the experiment.

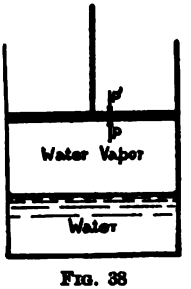


FIG. 38

The "solution pressure" of a substance, for example sugar, is

[1] *Ztschr. phys. Chem.*, 4, 129 (1889).

spoken of just as is the vapor pressure, and thereby is meant its tendency to pass into the dissolved state. This pressure may be measured in a manner similar to the measurement of vapor pressure. A diagram of the apparatus is shown in Figure 39. At the bottom of the vessel there is an excess of the solid substance, over which is its saturated solution, and a semipermeable piston, that is, one which is permeable to the water but not to the dissolved substance. Above the piston is pure water. If the piston be weighted, the magnitude of the load determines the direction in which the piston will move. If the load be less than the pressure derived from the dissolved particles, the "osmotic pressure," the piston will rise and water penetrate into the solution, which being thereby diluted, allows more of the solid substance to be dissolved. If it be greater, the piston sinks, and water passes from the solution. The latter becoming supersaturated, some of the solid substance separates out again. Under a certain weight the condition of equilibrium must exist and the piston remain stationary at any part of the cylinder. Evidently the relations are here exactly analogous to those of the vapor pressure of water, and the magnitude of the solution pressure of the substance at a given temperature is measured by the weight on the piston when in a condition of equilibrium.

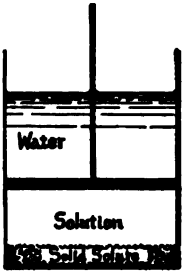


FIG. 39

It may here be repeated that, as made evident through these considerations, the vapor pressure of water being that pressure exerted by the vapor in contact with water, that is, the "saturated" vapor, so also the "solution pressure" of a substance is the osmotic pressure of the solution which is in equilibrium with the substance, that is, the "saturated" solution.

This conception may finally be applied to the passing of substances, chiefly in the case of elements, and especially metals, into the ionic condition. Hydrogen and the metals are capable of forming only positive ions; chlorine, bromine, iodine, etc., on the contrary, form only negative ions. The magnitude of this "electrolytic solution pressure" may be conceived as determined in exactly the same manner as the ordinary solution pressure. We imagine the substance in contact with water saturated with the ions in question, under a similar piston, which separates the saturated solution from the water, and is impermeable for the ions. The equilibrium with the osmotic pressure of the ions will be brought about by a certain weight of the piston, and no ions will enter the solution

from the substance nor pass out of solution. The weight of the piston in equilibrium represents the value of the *electrolytic solution pressure*, which is usually represented by P, and also expresses the equally great and oppositely directed osmotic pressure of the ions. This method is practically inapplicable, because in no case can appreciable amounts of positive or negative ions alone come into existence; this does not, however, affect the value of the conception.

In order to explain the production of a potential-difference through the contact of a solid substance with a liquid, imagine a metal dipped into pure water, and that a certain amount of metal ions is produced owing to the electrolytic solution pressure. The metal at the same time becomes negatively electrified, since both kinds of electricity must be simultaneously produced whenever electrical energy comes into existence. The solution is thus positively electrified and the metal negatively, and there is formed a so-called double-layer ("Doppelschicht") of electricities of opposite signs. [This is represented in Figure 40, in which the positive and negative ions are represented by plus and minus signs, respectively.]

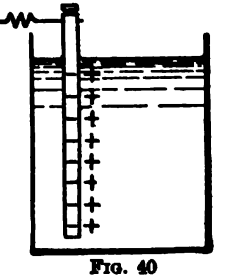


FIG. 40

The ions sent into the solution with positive charges and the negatively charged metal attract each other; in other words, a potential-difference is produced. The solution pressure constantly tends to send more ions into solution, while the electrostatic attraction of the electrical double-layer opposes this action, and evidently equilibrium is reached when the opposing tendencies are equal. Since the ions have very high charges of electricity, this condition of equilibrium occurs before weighable quantities of the ions have passed into the water. In the case of pure water the potential-difference, or strength of the electrical double-layer, depends only upon the magnitude of the solution pressure, but if the metal be in a solution of one of its salts, another factor is introduced, due to the metal ions already present. The osmotic pressure of these ions opposes the entrance of new ions of the same kind. It may occur that this osmotic pressure is exactly in equilibrium with the electrolytic solution pressure of the metal, consequently the latter will yield no ions and will not become negatively charged; in short, under these circumstances there will be no electrical double-layer produced. The nature of the negative ions of the salt in solution has no influence.

If the osmotic pressure of the metal ions differs from the electri-

cal solution pressure, two different cases may be distinguished according as the former or the latter is the greater. In the second case, ions pass from the metal into the solution as in pure water, and an electrical double-layer results. This action would evidently not be as great as in pure water, since so many ions cannot enter the solution, owing to the fact that the electrolytic solution pressure is opposed by the osmotic pressure of the ions already present. The quantities here involved are shown by the calculation made by Krüger.[1] In the case of zinc which is dipped in a solution which is of normal concentration in respect to Zn ions, 3.10^{-9} grams per square centimeter go into solution. In the other case ions separate from the solution and are precipitated upon the metal, communicating their positive electric charges to it. The metal thus becomes positively electrified, the solution, which formerly contained equivalent amounts of positive and negative ions, negatively electrified, and again the electrical double-layer is produced, the attraction of which opposes the previously superior osmotic pressure and adds itself to the solution pressure. This proceeds until the condition of equilibrium is reached. Here also the quantity of ions which is precipitated is unweighable. The strength of the electrical double-layer and the electrostatic attraction due to it is evidently dependent upon the osmotic pressure of the metal ions in the solution.

In all, three cases must then be distinguished:—

First, when $p = P$,

where p is the electrolytic solution pressure and P the osmotic pressure of the metal ions under consideration. Here equilibrium exists and no potential-difference or electrical double-layer is formed between solution and metal.

Second, when $p > P$.

In this case, the metal possesses a negative and the solution a positive charge of electricity. The electrostatic attraction opposes the solution pressure.

Third, when $p < P$.

Here the metal possesses a positive and the solution a negative charge. The electrostatic attraction is superposed on the solution pressure.

On turning our attention to the actual experimental facts, it is found, as will be seen later, that such base metals as the alkali metals, zinc, cadmium, cobalt, nickel, and iron, are always negatively charged when placed in solutions of their salts; the solution

[1] *Ztschr. phys. Chem.*, **35**, 18 (1900).

pressure in these cases is so great that, owing to the limited solubility of the salts, the osmotic pressure of the metal ions can never be raised to equilibrium with the solution pressure. On the other hand, with the noble metals, silver, mercury, etc., the metal is usually positively electrified in solutions of its salts. The solution pressure of the metals is here slight, and it is only by employing solutions containing very few of the ions in question, *i.e.* such as have very low osmotic pressure due to these ions, that it is possible to have the metal negatively charged in the solution.

With such substances as produce negative ions, *e.g.* chlorine, there is complete analogy. If the osmotic pressure of the chlorine ions is greater than the electrolytic solution pressure, ions pass into the condition of ordinary chlorine, and the "chlorine electrode" becomes negatively charged. In the other case the electrode becomes positively charged. As a matter of fact, as far as we know, all substances which produce negative ions have high solution pressures.

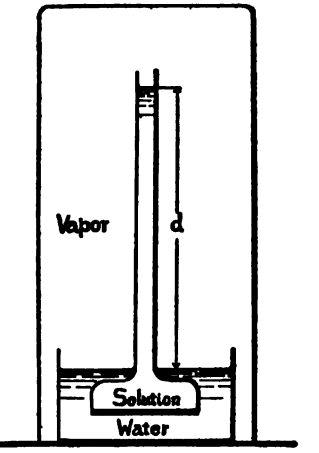


FIG. 41

So far the electrolytic solution pressure of a substance has been referred to as if it were a constant, but, just as with the vapor pressure and ordinary solution pressure, it is only constant under certain conditions, *i.e.* only when the temperature and the concentration of the electrode substance in question remains unaltered.

It is well known that the vapor pressure of water changes greatly with the temperature; but that it is affected by the concentration or density of the water itself, and is higher the greater this concentration, may be less commonly recognized. The fact may be recalled that if two open vessels containing water at different heights be allowed to stand in a confined space, the water distills from the higher level to the lower. The water in each vessel is under the pressure of the vapor above it, and these columns of vapor differ in height by the difference between the levels of the water surfaces. Consequently the system is not in equilibrium, the tendency being for vapor to condense under the greater pressure and be generated under the lower, which process continues until the surfaces of the water in the two vessels are at the same level, or that in one of the vessels is exhausted.

In the accompanying figure[1] the pure water and any water solution are separated by a membrane permeable to the water only. Under the conditions represented the liquids are in osmotic equilibrium, but the vapor pressure p_1 at the surface of the solution is less than that p of the water, and the equation $p_1 + w = p$ must represent the existing condition, where w is the weight of the column of vapor whose height is equal to the difference in level between the two liquids. If this were not true, water would distill from one surface to the other, thereby destroying the existing condition of osmotic equilibrium, and would also pass through the membrane in one direction in order to reproduce the osmotic equilibrium, etc. In short, a perpetual motion would result, by which *an unlimited amount of the heat of the surroundings at constant temperature could be transformed into work* (through the distillation of water vapor). This conflicts with the second law of energetics, and therefore is impossible.

If the upper end of the tube be closed by a membrane, allowing the passage of water vapor only, and a quantity of a gas insoluble in the liquid be placed between this membrane and the surface of the liquid, it will exert a certain pressure upon the latter, which will consequently sink to a lower level. The conditions of the equilibrium must again be that the vapor pressure p_1' at the surface of the solution, increased by the pressure of the column of water vapor d' between the two levels, is equal to the vapor pressure of the pure water p, or $p_1' + w' = p$. Evidently p has remained unaltered, d' is less than d, therefore p_1' is greater than p_1; that is, at the "compressed" surface, where the water is at the greater concentration, there is a higher vapor pressure than when the water is under a lower external pressure. The increase in the vapor pressure is evidently proportional to the pressure acting on the surface.[2]

Of the ordinary solution pressure it is also known that the concentration of the substances plays an important part. This is shown by Henry's law, in accordance with which the solubility of a gas, and therefore its solution pressure, since the two are synonymous, is to a great extent dependent upon the pressure, in other words, upon the concentration; it is, in fact, nearly proportional to the latter.

[1] *Ztschr. phys. Chem.*, **3**, 115 (1889).

[2] This conclusion was established by the work of Des Coudres and the author, which preceded the appearance of the article of Schiller on the same subject (*Wied. Ann.*, **53**, 396, 1894). The experiments in connection therewith were unavoidably interrupted and never concluded.

What has been said of vapor pressure and solution pressure applies equally well to electrolytic solution pressure, and accordingly there are cells possessing certain electromotive forces dependent only upon the different concentrations of the same ion-producing substances. It is true that usually but one condition of concentration for solid substances is recognized, and consequently only a single definite electrolytic solution pressure. But even here the concentration will be varied, as will be later described.

As in the case of the solubility, so the electrolytic solution pressure changes with a change in solvent. However, it has been shown by Luther[1] that the *relations between the solution pressures* of various metals are independent of the nature of the solvent, and, moreover, always possess the same value.

The electrolytic solution pressure varies with the temperature.

Calculation of the Electromotive Force existing at the Surface of Reversible Electrodes. — The potential-difference which appears when a reversible electrode is placed in contact with a liquid may easily be calculated according to the procedure given by Nernst. At the same time, the mathematical importance of the electrolytic solution pressure will be made evident.

Let us consider the following isothermal, reversible, cyclical process, noting first, however, that only the pressure of the corresponding ions come into consideration, *e.g.* in the case of a silver electrode, only the silver ions need be considered. Let π represent the desired potential-difference, and P the osmotic pressure of the univalent ions corresponding to the metal of the electrode.

Part 1. The quantity of electricity q is passed from the electrode into a solution of osmotic ion-pressure P, at a potential π. The quantity of work thereby obtained from the system is given by the equation

$$W' = \pi q.$$

Part 2. The equivalent of ions of volume V which has been formed in solution is now diluted reversibly to the volume $V + dV$, and the following quantity of work is obtained: —

$$W'' = P dV.$$

Quantities of work of the second order of magnitude have here been neglected.

Part 3. Since, in the above part, the volume has been increased

[1] *Ztschr. Elektrochem.*, **8**, 496 (1902). See also Brunner, *Ztschr. Elektrochem.*, 11, 415 (1905).

to $V + dV$, the osmotic pressure of the ions under consideration has been decreased to $P - dP$ and the potential-difference at the surface of contact of this diluted solution and the electrode has been increased to $\pi + d\pi$. Hence now when, under these new conditions, one equivalent of the ions is separated out of solution, the quantity of work consumed is as follows: —

$$W''' = (\pi + d\pi)\varrho.$$

The process is now complete and the quantities of work involved in the different parts may be summarized. Representing the work done by the system by a plus, and that done *upon* the system by a minus sign, then the sum must be equal to zero, or: —

$$\pi\varrho + PdV - (\pi + d\pi)\varrho = 0.$$

Hence
$$\varrho d\pi = PdV.$$

Since, according to Boyle's law, at constant temperature, —

$$PdV - VdP = 0, \text{ and } V = \frac{RT}{P},$$

it follows that
$$\varrho d\pi = -VdP = -RT\frac{dP}{P},$$

or, after integration,
$$\pi = -\frac{RT}{\varrho}\ln P + \text{const.}$$

Instead of the constant appearing in the last equation, the logarithm of another constant π, multiplied by $\frac{RT}{\varrho}$, may be substituted. This equation then becomes

$$\pi = -\frac{RT}{\varrho}\ln P + \frac{RT}{\varrho}\ln P = \frac{RT}{\varrho}\ln\frac{\pi}{P}.$$

When
$$\pi = P, \pi = 0,$$

and the constant π receives a comprehensible significance and is known as the *electrolytic solution pressure*.

If the ion is not univalent, but polyvalent, then the electrical work $v\pi\varrho$ per gram-ion is involved where v is the valency of the ion. The above equation then becomes

$$\pi = \frac{RT}{v\varrho}\ln\frac{\pi}{P}.$$

The quantity $\frac{R}{\varrho}$ is called the "electrolytic gas constant," and its value is
$$0.861 \times 10^{-4},$$

when the value of π is desired in volts.

Hence the above equation may be written as follows: —

$$\text{E} = \frac{0.861 \times 10^{-4}}{\text{v}} T \log \frac{\text{P}}{P} \text{ volts},$$

or, after multiplying by 2.3026,

$$\text{E} = \frac{0.0001983}{\text{v}} T \log \frac{\text{P}}{P} \text{volts}.$$

Referring the above equation to a room temperature of 18° t, then

$$T = 291°,$$

and the following equation is obtained,

$$\text{E} = \frac{0.05771}{\text{v}} \log \frac{\text{P}}{P} \text{ volts}.$$

This is a fundamental equation in the theory of reversible cells.

In considering a cell composed of two metals and two solutions, as, for instance, the Daniell cell,

$$\text{Zn} - \text{ZnSO}_4 \text{ solution} - \text{CuSO}_4 \text{ solution} - \text{Cu},$$

there are four places where potential-differences are produced: —

1. At the point of contact between the two metals,
2. At the point of contact between the two liquids,

3 and 4. At the points of contact of the two electrodes with the respective solutions.

The potential-difference at the point of contact between the two metals is so small that it may be usually left out of account. This is also often true of that existing between the two solutions. These magnitudes will shortly be calculated. Considering only the potential-differences at the points of contact of the electrodes with the liquids, the electromotive force of the cell at 18° is expressed by the following equation: —

$$\text{E} = \frac{0.05771}{\text{v}} \log \frac{\text{P}}{P} - \frac{0.05771}{\text{v}'} \log \frac{\text{P}'}{P'}.$$

P represents the electrolytic solution pressure of the one substance, the valence and osmotic pressure of whose ions are v and P; while P', V', and P' are the corresponding values for the other substance. The minus sign is used because at one electrode ions enter the solution, while at the other they pass from the solution; for example, in the Daniell cell zinc ions are produced, and simultaneously an equal number of copper ions separate at the other electrode; for the same number of positive and negative ions must always

be present in the solution. The investigation of special cases will now be taken up.

CONCENTRATION CELLS

1. Different Concentrations of the Substances which are Electromotively Active. — *a.* A cell formed of two differently concentrated amalgams of the same metal, for example zinc, in a solution of one of the salts of the metal, as zinc sulphate, possesses, according to the previous considerations, an electromotive force at $T°$ expressed by the equation,—

$$E = \frac{0.0001983}{2} T \log \frac{P}{P} - \frac{0.0001983}{2} T \log \frac{P'}{P},$$

where P and P' represent the electrolytic solution pressure of the zinc in the concentrated and in the dilute amalgam, respectively, and P the concentration of the zinc ions in the solution. Since the latter concentration is the same throughout the solution, the above equation may be simplified to

$$E = \frac{0.0001983}{2} T \log \frac{P}{P'} \text{volts.}$$

Dilute amalgams may be considered to be solutions in which the mercury is the solvent and, in the above case, zinc the dissolved substance. The zinc, like all dissolved substances, exerts a certain osmotic pressure which, since the amalgams are not of the same concentration, is different at the two electrodes. Since these are proportional to the concentrations, the electrolytic solution pressures of the amalgams may be assumed to be proportional to the osmotic pressures of the dissolved zinc.[1] From this

$$E = \frac{0.0001983}{2} T \log \frac{C}{C_1} \text{volts,}$$

where C and C_1 are the concentrations of the zinc in the amalgams. That values of E calculated in this manner agree with those experi-

[1] This is equivalent to assuming that the dissolved substance is present in the mercury as atoms, which will be demonstrated from a consideration of concentration cells formed from gases. If it be assumed that a compound is formed between the mercury and the substance dissolved in it of the type $X \cdot Hg_n$, then another term must be added to the above equation. Since this term is within the limits of experimental error, the question of the formation of such a compound remains unanswered. It must at least be concluded from the experiments, either that the molecules of dissolved substance are monatomic, or that they are combined singly with the solvent, mercury.

mentally determined may be seen from the following results obtained by G. Meyer:[1] —

Zinc Amalgam and Zinc Sulphate Solution

t	C	C_1	E found	E calculated
11.6°	0.003366	0.00011305	0.0419 volt	0.0416 volt
18.0°	0.003366	0.00011305	0.0433 volt	0.0425 volt
12.4°	0.002280	0.0000608	0.0474 volt	0.0445 volt
60.0°	0.002280	0.0000608	0.0520 volt	0.0519 volt

Cadmium Amalgam and Cadmium Iodide Solution

t	C	C_1	E found	E calculated
16.3°	0.0017705	0.00005304	0.0433 volt	0.0440 volt
60.1°	0.0017705	0.00005304	0.0562 volt	0.0507 volt
13.0°	0.0005937	0.00007035	0.0260 volt	0.0262 volt

Copper Amalgam and Copper Sulphate Solution

t	C	C_1	E found	E calculated
17.3°	0.0003874	0.00009587	0.01815 volt	0.0176 volt
20.8°	0.0004472	0.00016645	0.0124 volt	0.0125 volt

The electromotive force E of such cells can be calculated in a second way, independent of the idea of electrolytic solution pressure. The action of the cell consists in zinc passing from the more concentrated amalgam into the solution, and at the same time from the solution into the weaker amalgam. As a result of the whole action, zinc is transferred from the concentrated to the dilute amalgam, or, in other words, zinc at an osmotic pressure P, or the proportional concentration C, changes to the osmotic pressure P_1, or the concentration C_1. The maximum amount of work thereby obtainable osmotically is

$$W = \frac{RT}{0.4343} \log \frac{C}{C_1},$$

for a gram-atom, when the metal is assumed to be present in the mercury in the form of atoms.

The value of the work obtained electrically from the same process is $2 \times 96540 \times E$, and since the two maximum quantities of work must be equal,

$$2 \times 96540 \times E = \frac{RT}{0.4343} \log \frac{C}{C_1},$$

[1] *Ztschr. phys. Chem.*, 7, 447 (1891), and Ostwald, *Allgem. Chem.*, II, 1, 861.

or $$\pi = \frac{0.0001983}{2} T \log \frac{C}{C_1} \text{ volts.}$$

This is the same formula obtained by the previous method, and will also be used later in the calculation of π.

It was assumed that the metal is present in the mercury in the atomic state, and since the experimentally determined values of π agree with those calculated, this assumption may be considered justified.

If the metals had dissolved in the mercury in complexes of two atoms each, the work obtainable osmotically, through the transference of the same amount of metal as before, would have been

$$W = \frac{1}{2} \cdot \frac{RT}{0.4343} \log \frac{C}{C_1},$$

because the number of separate particles to be transferred is only half as great. The work obtainable depends upon their number, but not upon their weight. The corresponding electrical energy would be

$$2 \times 96540 \times \pi',$$

therefore $$2 \times 96540 \times \pi' = \frac{1}{2} \frac{RT}{0.4343} \log \frac{C}{C_1},$$

and $$\pi' = \frac{1}{2} \cdot \frac{0.0001983}{2} \log \frac{C}{C_1} = \frac{1}{2}\pi;$$

or in such a case the electromotive force of the cell would be only half as great as is actually found. The monatomic character of the metal molecules in mercury solutions has also been proved from measurements of the vapor-pressure lowering.

As shown by the equation, π depends only upon the relation between the concentrations and upon the valence of the metal, and is in other respects independent of the nature of the metal.

The amalgams have been considered simply as differently concentrated zinc electrodes; it might be asked if the mercury in them does not also play the part of an electrode, and its electrolytic solution pressure come into consideration. In order to dispose of this question at once, it may be stated that, in the case of electrodes composed of two or more metals, three cases are recognized.[1]

Case 1. If the metals form a *mechanical mixture*, the potential will be that of the least noble metal. Such a mixture of metallic zinc

[1] Herschkowitz, *Ztschr. phys. Chem.*, **27**, 123 (1898); Ogg, *Ztschr. phys. Chem.*, **27**, 285 (1898); Haber, *Ztschr. Elektrochem.*, **8**, 541 (1902); Reinders, *Ztschr. phys. Chem.*, **42**, 225 (1902).

and metallic cadmium, for example, when used as the negative electrode of a cell containing acid, sends practically only zinc ions into the solution. The electromotive force is, therefore, at first that of pure zinc.

If zinc ions be added to the solution, but little effect is produced. Only a small quantity of cadmium dissolves. On the other hand, if cadmium ions be added to the solution, a considerable secondary reaction results. This proceeds until such a number of cadmium ions have been deposited and replaced by zinc ions as will make the potential-difference between the zinc and the zinc ions equal to that between the cadmium and the cadmium ions. When this has occurred, again practically only pure zinc goes into solution.

The above-mentioned equality of the potential-differences between the metals and the solution is, under all circumstances, spontaneously established, *i.e.* a local action takes place until it is established. Since the individual potential-differences depend upon the relation between the electrolytic solution pressure and the osmotic pressure of the corresponding ions, evidently in the case of equi-valent metals, the osmotic pressures of the corresponding ions must be related to each other as the solution pressures, in order that equality of potential-difference may be attained. In the case of great differences in the solution pressures, as, for example, between zinc and cadmium, the concentration of the cadmium ions must be extremely small as compared with that of the zinc ions. Since, because of the extreme smallness of the former concentration, it is greatly changed by the addition of new quantities of cadmium ions, while the latter concentration is but slightly changed by the addition of a far greater quantity of zinc ions, it is evident that, if the potential-differences must remain the same, practically only zinc ions will go into solution.

In the case of a mixture of two equi-valent metals which possess the same electrolytic solution pressure, equilibrium is only established when the two corresponding ion concentrations are equal, *i.e.* when the two metals dissolve to the same extent in the solution.

Case 2. If the metals form a *solution* (amalgam or alloy), the latter is always more noble than the least noble component, and, further, this is true to a greater extent, the greater the loss in free energy accompanying the formation of the alloy. It may even happen that the metallic solution is more noble than the noblest component.

The solution or dissolving of such alloys takes place in a manner analogous to that already outlined. In all cases, the potential-

differences between the alloy of the least noble metal and the ions of this metal, and between the alloy of the more noble metal and the ions of this metal, must be equal to each other. It is to be noted, however, that this potential-difference is not the same as that which would exist between the pure metals and the same solution, and, further, that because of the dependence of the electrolytic solution pressure upon the concentration of the metal in the alloy, it changes with the composition of the alloy. If the solution pressures of the two alloyed metals differ very greatly, as is usually the case, then the least noble metal is practically the only one which dissolves in the solution.

Case 3. If, finally, the metals form a chemical compound with each other, and if this compound can exist as such in the solution, which contains a definite quantity of the metal ions corresponding to the constituent metal of the compound, as, for example, copper and zinc ions in the case of a zinc-copper compound, then this compound possesses its own electrolytic solution pressure. From this it must be concluded that during the solution of the electrode, ions of the same composition as the electrode are sent into the solution, where they eventually are dissociated to a large extent into the individual components. In this case, the potential-difference is dependent upon the product of the concentrations of these individual ions.

To avoid errors in the interpretation of the phenomena, it must be borne in mind that only the composition of the layer of the electrode which is in direct contact with the electrolyte is of influence upon the electrolytic solution process. The composition of this layer, in the case of a solid alloy, may change by the gradual solution of the less noble metal alone. Since an appreciable diffusion cannot take place, the more noble metal remains alone upon the surface of the electrode. Hence it is that such an alloy exhibits, after a time, the potential and other properties of the more noble metal.

Advantage is taken of the fact that the least noble metal dissolves first, in the preparation of pure metal surfaces. When a metal containing a quantity of a less noble metal is placed in a solution of one of its salts, the latter metal goes into solution accompanied by the deposition of some of the former metal from the solution. In this manner, it is possible to free the entire mass of mercury from the less noble metals dissolved in it.

The same principles play a very important part in the commercial purification of metals. For example, copper is purified by placing the impure copper plate, as an anode, in an acid solution of copper

sulfate of a certain concentration, near a suitable cathode, upon which the pure copper is to be deposited. When, now, an electric current is passed through the cell thus formed, the less noble metals contained in the impure copper plate dissolve first, but do not, as will be shown in the chapter on electrolysis and polarization, deposit upon the cathode. Thereafter the copper goes into solution. When the impure anode plate is nearly consumed, what remains of it is composed of copper, and the more noble metals, silver and gold. The latter metals have, then, been concentrated partly in the remains of the anode and partly in the anode mud which falls from the anode during the electrolysis. Thus not only is the copper purified by this process, but also the more noble metals are so concentrated that they may easily be obtained in the pure state.

The important practical question as to whether iron is better protected by a coating of a more, or of a less, noble metal, *e.g.* by a coating of copper or of zinc, can now be considered. As long as only impenetrable coatings are to be considered, that one would naturally be chosen which best resists the action of the atmosphere. Of the two metals just mentioned, copper would be preferred. On the other hand, if coatings which are penetrable, as are all coatings in practice, are to be considered, then, since moisture is always present, at the points of penetration there will be a mixture of two metals in contact with a liquid. According to the principles already studied, at these points the less noble of the two metals will be acted on by the moisture. Hence if the iron is covered with zinc, as long as the zinc remains it will dissolve and protect the more noble metal, iron, while if the iron be covered with copper, it is not at all protected thereby, but, on the other hand, its corrosion is accelerated.

From the same point of view, the fact that aluminium cannot be durably soldered may be explained. Since only the more noble metals are suitable for soldering, in the case of such a metal as aluminium a galvanic cell is formed at the soldered points which, when in action, causes the aluminium to go over into the ionic state. The aluminium thus dissolved finally becomes oxidized to aluminium oxide, forming the observed fungus-like growth.

b. The combination,

Hg — Hg (-ous) salt solution — Amalgam of a noble metal,

can also be classed as a concentration cell. It is evident from the discussion in the previous section that in this cell the mercury is present in different concentrations at the two electrodes. Naturally only those metals may be used to dilute the mercury whose solution

pressure is less than that of the mercury, as, for example, the so-called noble metals, gold and platinum. A mercurous salt must be used as the electrolyte. Murcuric salts are immediately reduced to the mercurous state when brought into contact with metallic mercury, according to the equation —

$$Hg^{\cdot\cdot} + Hg = 2\ Hg^{\cdot}.$$

The electromotive force of this mercury concentration cell may be easily calculated, as was that of the previously described cell, either with or without the use of the idea of electrolytic solution pressure. It will be sufficient to apply the shorter method, since the electromotive force of such a cell has not yet been experimentally determined.

During the action of the cell, mercury dissolves from the pure mercury electrode, where the solution pressure is greater, and is precipitated upon the amalgam electrode. The maximum work available osmotically will now be calculated and placed equal to the maximum available electrical work.

Let us consider a system such as is shown in Figure 42, in which the pure solvent, mercury, is separated from the solution of a metal in mercury, the amalgam, by a movable semipermeable piston. Let P represent the osmotic pressure of the solution, and V the volume of it which contains one mol of the dissolved metal. Now let the semipermeable piston be moved downward under the constant pressure p, from the point a to the point b, whereby the volume V of the pure solvent enters the solution. If, for example, this volume is one cubic meter, then one cubic meter of the solvent passes through the piston into the solution, and the piston is moved through the volume of one cubic meter at the constant pressure p. Finally, let the volume of the solution be so great that the introduction into it of the volume V of the solvent causes no appreciable change in its concentration. Since V is the volume of the solution containing one mol of the dissolved substance, the maximum quantity of work which can thus be obtained is as follows: —

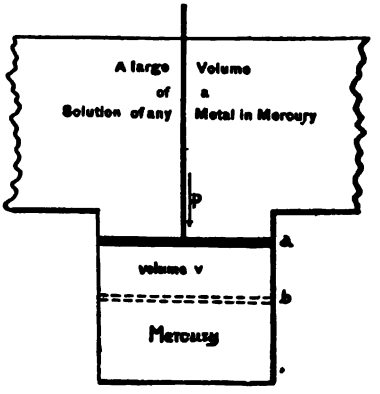


FIG. 42

$$W = PV.$$

But $PV = RT,$

and consequently $W_o = RT,$

where W_o represents the maximum quantity of work obtainable osmotically. In order to obtain the equivalent electrical energy of work, the number of equivalents of mercury (n) contained in the volume V must be dissolved at one electrode and deposited at the other electrically. The electrical work is then given by the equation,

$$W_e = n\text{F}\mathfrak{q};$$

therefore $$n\text{F}\mathfrak{q} = RT,$$

or $$\text{F} = \frac{RT}{n\mathfrak{q}}.$$

The values of R, T, and $\mathfrak{q}$ are known, and that of n, the number of equivalents of mercury containing one mol of dissolved metal in the amalgam, may be found. Hence the value of F is easily calculated.

This method serves also for determining the molecular weight of the noble metals dissolved in the mercury; n is the number of mols of mercury containing one mol of the dissolved metal. By measuring F, n is obtained, and from the known concentration of the amalgam, the weight of the dissolved substance in n, which represents the molecular weight, is calculable.

c. A second mercury concentration cell is the following: —

Mercury ($p > p_a$) — Mercurous salt sol. — Mercury ($p = p_a$),

where p and p_a represent the pressure upon the mercury and the atmospheric pressure respectively. [It is shown in Figure 43.] In such a cell mercury passes from the former electrode through the electrolyte to the latter. Des Coudres[1] arranged this cell as follows: A column of mercury of height d formed one electrode; the lower end of the tube containing it, closed by means of parchment paper, was placed in a salt solution. The paper was impervious to the mercury as such, but allowed the passage of it in the form of ions. The surface of the second mercury electrode

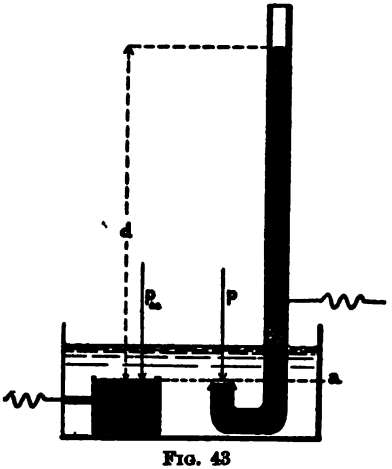


FIG. 43

[1] *Wied. Ann.*, 46, 292 (1892).

was at the level of the parchment membrane. The height of the mercury column decreases by a definite amount when a mol of mercury passes from the electrode under pressure p to the other under the pressure p_{∞}. The maximum work thus obtainable may be calculated, and placed equal to the electrical energy involved. The work necessary for the transference of the ions through the solution may be left out of account. If 200 grams thus leave the column of mercury, which is of great height d, the effect is the same as though 200 grams of mercury had fallen the distance d. The maximum available mechanical energy is 200 d gram-centimeters, where d is expressed in centimeters. Therefore, since, according to page 17, gram-centimeter units must be divided by 10,198 in order to obtain electrical units,

$$\text{FQ} = \frac{200\,d}{10198},$$

and the electromotive force has the value given in the following equation: —

$$\text{F} = \frac{200\,d}{96540 \times 10198} \text{ volts.}$$

In the following table, experimentally determined values are compared with those calculated with the aid of the above equation: —

Pressure in cm.	F calculated	F found
36	7.2×10^{-6} volts	7.4×10^{-6} volts
46	9.3×10^{-6} volts	10.5×10^{-6} volts
113	23×10^{-6} volts	21×10^{-6} volts

Considering the difficulty of accurately measuring these small values, the agreement must be considered satisfactory.

In this connection, it is of interest to inquire the value of the electromotive force which would be obtained if the above experiment be so changed that mercury columns of the same height but situated at different levels in the solution are used as electrodes. If the difference between the levels of the two electrodes is equal to d centimeters, will the electromotive force be the same as in the former experiment? As before, by the passage of one mol of mercury from the higher to the lower electrode, the following maximum quantity of work can be obtained: —

$$W = 200\,d \text{ gram-centimeters.}$$

Nevertheless, in answer to this question, it may be stated that the electromotive force of the latter must always be less than that of the former cell, and that, moreover, under certain circumstances the direction of the current may even be reversed. This is due to the fact that the migration downward of the mercury ions necessitates the corresponding migration upward of the negative ions, which latter requires the expenditure of work. As long as the mass of negative ions migrated upward is less than that of the positive ions migrated downward, an electric current flows through the solution from the lower electrode. When, however, the mass of the negative is the greater, work may be obtained through the migration downward of the negative ions and the corresponding migration upward of the positive ions. In this case the direction of the electric current is reversed, *i.e.* the current flows through the solution from the lower to the higher electrode. It is evident that here the transference number, as well as the mass, of an ion plays an important part, and, moreover, that a deficiency in mass of a given ion may be compensated by a greater speed of migration.

Recent investigations carried out by R. R. Ramsay[1] on the influence of gravity upon electrolytic phenomena have confirmed the above conclusions. For example, in the case of a ten per cent solution of zinc sulfate, the current flows through the solution from the lower to the upper zinc electrode. This would be expected, from the fact that while 32.5 grams of zinc are migrated upward in a given time, 57.7 grams of sulfate ions are migrated downward.

After this experience, the fact that when two pieces of the same metal, in which respectively the metal exists in different modifications, or in which it possesses *any difference in physical structure or quality*, are dipped into a solution and then brought into contact, an electric current is produced, is no longer particularly wonderful. Thus iron which has been subjected to tension or pressure possesses a greater electrolytic solution pressure than ordinary iron. The recognition of this fact is of importance in so far as it furnishes an explanation for the very active corrosion at certain places on iron cables and boiler plates. It may be stated in general that iron which has been subjected to an uneven strain, or which has not been uniformly treated, corrodes more readily than does iron which has been treated uniformly; and, further, that highly polished corrodes less readily than unpolished or poorly polished iron.[2]

Since the transformation of an unstable form, or a form which is

[1] *Ztschr. phys. Chem.*, 41, 121 (1902).

[2] *Jahrbuch der Elektrochemie*, 8, 224 (1902).

produced by the action of an external force, into the form which is stable under ordinary conditions, is a process which takes place spontaneously, and which is capable of producing work, the electric current always flows in such a direction that the unstable may pass over into the stable form.

d. Finally, concentration cells may be produced from gases, or aqueous solutions of different concentrations, as ion-producing substance. At the first glance it may seem improbable that gases or liquids, which possess no metallic conductance, can serve as electrodes. [Nevertheless, by means of a special arrangement, such as is represented in Figure 44, this end is easily attained.] A platinized platinum electrode (Pt) is passed into a tube which is afterward closed, so that its lower end extends into a liquid. The tube is so filled with the gas under consideration that the platinum plate is for the greater part in the gas, the remaining portion being in the liquid. The platinized platinum absorbs a certain quantity of the gas, and may then be considered as a gas electrode. The only other part the platinum plays in these cells is that of conductor of the electricity. Because of its power of dissolving the gases the platinum permits the change from the gaseous to the ionic state, and the reverse, without resistance. Such an electrode, *e.g.* one of hydrogen, belongs to the reversible class, as has been experimentally shown by Le Blanc.[1] The quantity of work developed by the passage of a certain quantity of gas into the ionic condition is exactly the quantity necessary and sufficient to produce the reverse action. Since this is true, the material of the metallic electrode can have no effect upon the electromotive force, and, in fact, equal values have been obtained with platinum and palladium electrodes.

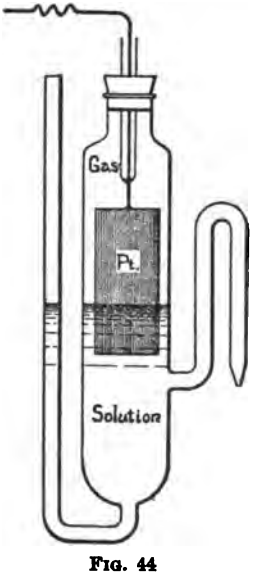


FIG. 44

By means of such platinized platinum electrodes, reversible hydrogen, oxygen, chlorine, bromine, and iodine electrodes may be prepared. By arranging a reversible cell of two such electrodes, using as ion-producing material the same substance for each, but in different concentrations, a concentration cell entirely analogous to that of the amalgam results. The electrolyte to be used must evidently be

[1] *Ztschr. Phys. Chem.*, **12**, 333 (1893).

one containing the same ions as the gas produces. If, for example, hydrogen be the gas, an acid must be used; if oxygen, the corresponding ions of which are OH (or O ions), a solution of a base must form the electrolyte. This kind of a cell is independent of the nature of the electrolyte, except for the above consideration defining one of the ions.

In the calculation of the electromotive force of a gas cell, for example one consisting of two hydrogen electrodes under the pressures p and p_1, the process is the same as with the amalgam cell, except that it must be borne in mind that the hydrogen molecule contains two atoms. In the reversible change of one mol of hydrogen from the pressure p to p_1, the maximum work is represented by

$$RT \ln \frac{p}{p_1}.$$

The corresponding energy, when the process is considered as an electrical one, is $2\,\mathrm{E}\underline{\mathrm{Q}}$ because one molecule of hydrogen produces two univalent ions; therefore

$$\mathrm{E} = \frac{RT}{2\,\underline{\mathrm{Q}}} \ln \frac{p}{p_1}.$$

The factor 2 occurs here in the denominator, even though the equation applies in this case to univalent ions.

If the calculation be made in accordance with the osmotic process, using solution pressures as on page 184, the equation is

$$\mathrm{E} = \frac{RT}{\underline{\mathrm{Q}}} \ln \frac{\mathrm{P}}{\mathrm{P}_1},$$

P and P_1 being the solution pressures of the gas corresponding to the pressures p and p_1 respectively. Evidently the two must be equal,

or
$$\frac{RT}{2\underline{\mathrm{Q}}} \ln \frac{p}{p_1} = \frac{RT}{\underline{\mathrm{Q}}} \ln \frac{\mathrm{P}}{\mathrm{P}_1},$$

and
$$\frac{1}{2} \ln \frac{p}{p_1} = \ln \frac{\mathrm{P}}{\mathrm{P}_1};$$

therefore
$$\frac{p}{p_1} = \frac{\mathrm{P}^2}{\mathrm{P}_1^2}.$$

That is, the squares of the solution pressures are in the same ratio as the corresponding gas pressures. This result is not difficult to understand. It may be recalled that P and P_1 represent osmotic pressures (page 177). If the osmotic pressure P exists in a solution

at the one gas electrode whose gas pressure is p, while at the other the osmotic pressure is P_1 and the gas pressure p_1, there is no potential-difference at the electrodes. There is a condition of equilibrium between the gas molecules H_2 and the corresponding ions $H^{\cdot}$. When such a condition exists that the undissociated portion H_2 and the dissociated portions $H^{\cdot} + H^{\cdot}$ are in equilibrium, the concentration of the undissociated portion, divided by the product of the concentrations of the dissociated portions, is a constant.

$$\frac{C_{H_2}}{C_{H^{\cdot}} \times C_{H^{\cdot}}} = K_4.$$

Moreover, the gas and osmotic pressures are proportional to the concentration, hence

$$\frac{p}{P^2} = K,$$

and also

$$\frac{p_1}{P_1^2} = K;$$

therefore

$$\frac{p}{p_1^2} = \frac{P^2}{P_1^2}.$$

Recently quantitative measurements of the electromotive force of such cells have been made, the results of which are in agreement with the predictions. A somewhat complicated case will now be considered.

A hydrogen sulfide concentration cell has been investigated by Bernfeld.[1] Hydrogen sulfide dissociates according to the equation,

$$H_2S \rightleftarrows H^{\cdot} + HS',$$

and to an extremely slight extent according to the equation,

$$H_2S \rightleftarrows 2\,H^{\cdot} + S'',$$

and always in such a manner that an equal number of positive and negative ions are formed. Hence it is evident that this gas would produce no current in such an arrangement as is used for the hydrogen concentration cell. However, by means of an artifice, a reversible hydrogen sulfide concentration cell can be made.

The following reaction takes place between hydrogen sulfide and lead sulfide: —

$$H_2S + PbS \rightleftarrows Pb + 2\,HS'.$$

[1] *Ztschr. phys. Chem.*, 25, 46 (1898).

If now two lead electrodes which have been covered with a thin layer of lead sulfide be partially submerged in a solution of sodium sulfhydrate of a definite concentration and partially enveloped by hydrogen sulfide gas of different concentrations, two systems are obtained which, with the exception of the concentrations of the hydrogen sulfide gas, are identical. Upon connecting the two electrodes thus formed by means of a wire, an electric current is obtained. As the current passes, the hydrogen sulfide gas under the greater pressure enters the following reaction: —

$$H_2S + PbS \rightarrow Pb + 2\,HS';$$

while at the other electrode, the following reaction occurs: —

$$2\,HS' + Pb \rightarrow PbS + H_2S.$$

Since in this cell negative ions form and disappear, the direction of the current is the reverse of that of the hydrogen cell. The values of the electromotive force of the two cells are, however, the same when the respective gases are maintained under the same pressures. That of the hydrogen sulfide cell is as follows: —

$$-E = \frac{RT}{2\varrho} \ln \frac{P_{H_2S}}{P'_{H_2S}}.$$

It is evident that the nature of metal sulfide forming the electrodes does not come into consideration, and it would be expected, therefore, that the same value of the electromotive force would be obtained if, instead of the lead-lead sulfide, silver-silver sulfide or bismuth-bismuth sulfide electrodes were used. This conclusion is well confirmed by the results contained in the following table: —

Electrodes =	Pb – PbS			Ag – Ag_2S		Bi – Bi_2S_3		
$\frac{P_{H_2S}}{P'_{H_2S}}$ =	37.50 / 15.56	37.61 / 6.26	37.44 / 12.91	35.1 / 4.2	34.6 / 5.2	37.50 / 1.71	37.50 / 4.27	37.50 / 2.92
Millivolts calc. =	−11.0	−22.4	−13.3	−26.6	−23.7	−38.6	−27.2	−34.3
Millivolts found =	− 8.9	−21.1	−10.9	−25.0	−21.4	−36.8	−25.8	−32.7

The consideration of a second kind of concentration cell will now be taken up.

2. Different Concentrations of the Ions.—(*a*) The combination,

$$Ag - AgNO_3 \text{ sol., dilute} - AgNO_3 \text{ sol., concentrated} - Ag,$$

may be considered as a type of these cells. In such a cell, where

the electrode furnishes positive ions, the current always flows through the cell (not through the external circuit) from the dilute to the concentrated solution. Silver is dissolved into the dilute solution and precipitated from the other, this process continuing until the two solutions become of the same concentration. That the silver ions must precipitate from the more concentrated solution is evident when it is remembered that the osmotic pressure here directed against the solution pressure is greater than in the dilute solution. If the electrodes furnish negative ions, then the current flows through the cell from the solution most concentrated, to that most dilute, in respect to the negative ions. It will be remembered that by current direction is meant the direction in which the positive ions migrate.

Leaving out of account for the present the potential-difference which exists at the point of contact between the two solutions, the electromotive force of such a cell is given by the equation,

$$\pi = \frac{RT}{\mathfrak{Q}} \ln \frac{p}{P_1} - \frac{RT}{\mathfrak{Q}} \ln \frac{p}{P},$$

where p is the electrolytic solution-pressure of silver, and P and P_1 are the osmotic pressures of the silver ions in the concentrated and the dilute solution, respectively. Since the solution pressures are the same, the formula may be simplified to

$$\pi = \frac{RT}{\mathfrak{Q}} \ln \frac{P}{P_1}.$$

This expresses the fact that the electromotive force of such a cell is dependent only upon the relation between the osmotic pressures and upon the valence of the metal ions, and is independent both of the nature of the metal and of the negative ions of the electrolyte.

The electromotive force may also be ascertained by the second method, through calculating the maximum of energy represented by the osmotic change when one ion equivalent of silver migrates from one electrode to the other. For this purpose the conditions of the cell before and after the electrolysis are compared.

If one ion equivalent of silver dissolves in the dilute solution, the silver concentration is increased by one ion equivalent, but at the same time some silver also passes from the dilute to the concentrated solution. If $(1 - n_a)$[1] be the transference number of the silver, $1 - n_a$ ion equivalents leave the dilute solution, and the actual

[1] See page 70.

increase in the concentration of the latter when one ion equivalent dissolves is n_a ion equivalents. The more concentrated solution must evidently have its concentration reduced by this amount. A migration of NO_3 ions also takes place. If n_a represent the share of transport for this ion, then $n_a NO_3$ ion equivalents pass from the concentrated to the dilute solution, since the motion is in the direction opposite to that of the silver ions. Consequently $1 - n_a$ ion equivalents of silver and the same number of ion equivalents of NO_3 move from the concentrated solution to the dilute during the passage of 96,540 coulombs, *i.e.* from osmotic pressure P to P_1. The relation of the osmotic pressures of the anions as well as of the cations is $\frac{P}{P_1}$. The work is expressed by the equation,

$$W = 2 n_a RT \ln \frac{P}{P_1},$$

and

$$E = \frac{2 n_a RT}{\mathfrak{Q}} \ln \frac{P}{P_1}.$$

On comparing this equation for the electromotive force in the case of univalent metals with that obtained above, it is seen that when $n_a = \frac{1}{2}$, *i.e.* when the two ions have equal velocities of migration, the equations become identical. When this is not the case, a potential-difference exists (see later) at the point of contact between the solutions, and this requires the application of a correction to the previous equation; consequently the formula just derived is more general in its application. It will be assumed for the present that $n_a = \frac{1}{2}$.

The following formula is the most general one: —

$$E(v\mathfrak{Q}) = n_i n_a RT \ln \frac{P}{P_1},$$

or

$$E = \frac{n_i n_a}{(v\mathfrak{Q})} RT \ln \frac{P}{P_1}.$$

Here $v\mathfrak{Q}$ is the quantity of electricity which must flow through the cell in order to cause n_a mols of the electrolyte to pass from the concentrated to the dilute solution. The highest valency represented by the ions in a given case gives the value of v directly. If zinc chloride be the electrolyte, $v = 2$. In the concentration cell,

$$Tl - Tl_2SO_4 \text{ sol., conc.} - Tl_2SO_4 \text{ sol., dilute} - Tl,$$

v is also equal to 2. If the electrolyte be thallium nitrate, $v = 1$,

and so on. The number of ions formed from a molecule of the electrolyte is n_i.

For dilute solutions the relation between the concentrations may be used, instead of that between the osmotic pressures. For example, in the cell,

$$Ag - AgNO_3 \text{ sol., } 0.01\ C_n - AgNO_3 \text{ sol., } 0.001\ C_n - Ag,$$

the value 10 may be substituted for $\frac{P}{P_1}$ in the equation, and the value of the electromotive force so obtained should agree closely with that measured.

Nernst[1] measured the electromotive force of the cell,

$$Ag - AgNO_3 \text{ sol., } 0.1\ C_n - AgNO_3 \text{ sol., } 0.01\ C_n - Ag,$$

and found, at 18° t, $\qquad E = 0.055$ volt.

From conductivity measurements, it was calculated that the ratio of the two concentrations of silver ions, instead of being 1 : 10 was 1 : 8.71. Hence the calculated value of the electromotive force is as follows: —

$$E = 0.000198 \times 291 \log 8.71 = 0.054 \text{ volt.}$$

In this calculation it was assumed that the transference numbers of the anion and cation are equal. If the fact that, instead of the two values being equal, the value of the transference number of the nitrate ion is 0.53 is taken into consideration, the calculated value of the electromotive force becomes

$$E = 0.057 \text{ volt.}$$

Hence the agreement between the calculated and the experimentally found value is very satisfactory.

The following statements will serve to give a general idea of the magnitude of the numerical values. Since at 17°, when

$$n_i = 2 \text{ and } n_s = 0.5,$$

$$E = \frac{0.0575}{v} \log \frac{P}{P_1} \text{ volts,}$$

it follows, where the concentrations of the ions to be considered are in the ratio 1 : 10 and the metal univalent, that

$$E = 0.0575 \text{ volt.}$$

[1] *Ztschr. phys. Chem.*, 4, 129 (1889).

If the ratio of the concentrations is increased to 1 : 100 or 1 : 1000, the value of E becomes twice or three times as great, since E increases in logarithmic ratio.

It may be stated in general, that if a concentration cell involving univalent ions possesses an electromotive force,

$$E = a \times 0.0575,$$

under the conditions stated above, the ratio of its ion concentrations is,

$$\frac{C}{C_1} = 10^a.$$

If the ion be other than univalent, the corresponding values must be divided by the valency. Thus the cell consisting of copper and copper sulfate solutions, in which the concentrations of the copper ions are 1 : 10, would give an electromotive force of about one half that of the corresponding silver concentration cell. Measurements by Moser corroborate this statement.

The equation used above for the calculation of the electromotive force, which is sometimes known as the Nernst equation, appears to hold, not only for aqueous solutions, but also for solutions in fused salts. At least, Gordon[1] has measured the electromotive forces of different concentration cells of silver nitrate, dissolved in a fused mixture of potassium and sodium nitrates, at temperatures between 200° and 300° *t*, and found that the values of the electromotive force calculated by means of the above equation, under the assumption of complete dissociation, agree with the values found by experiment. He observed further, that when the concentration of the silver nitrate was greater than ten per cent, the value found by experiment was always less than the calculated value. This indicates an appreciably incomplete dissociation at this concentration.

Concentration cells are involved in most electrolytic work, especially in metal refining and in galvanoplastic work. In these cases the solution becomes more concentrated about one electrode, and less concentrated about the other. When the stirring is insufficient, the electromotive force of the concentration cell which results may be of a considerable magnitude. Since this force must be overcome by the electromotive force of the primary current, energy is thus unnecessarily lost. Furthermore, disturbances due to the decrease in the ion concentration about the cathode may injure the quality of the deposition of metal. Concentration cells may even be formed

[1] *Ztschr. phys. Chem.*, **28**, 302 (1899).

at one electrode alone when the current is not evenly distributed. Such cells may make themselves unpleasantly evident by causing the metal already deposited to redissolve in places. This is confirmed by the following simple experiment: If a dilute layer is placed above a concentrated layer of stannous chloride solution in a test tube containing a rod of tin, it will be observed that the part of the rod in contact with the dilute solution is very soon eaten into, while crystals of tin separate out on the part in contact with the concentrated solution. The formation of concentration cells at one electrode can be prevented by an efficient stirring of the solution.

The fact that standard cells can only be used for small current densities may now be understood. Because of the slight solubility of the mercury salts used in them, the concentration of the ions is very small. Moreover, the ions removed from the solution by the passage of the current are but slowly replaced from the excess of solid salt. Consequently, the electromotive force of the cell must decrease when it produces a considerable current. While at the cathode a state of under saturation is produced, at the anode the solution becomes slightly supersaturated. When the cell is allowed to remain inactive for a time, the concentrations of the solution about the two electrodes change spontaneously until the original uniform value is reached. This discussion leads directly to the consideration of a second kind of concentration cells.

b. A type of this kind of concentration cells is represented by the combination,

$$Ag - AgNO_3 \text{ sol.} - KCl \text{ sol.} - Ag \text{ (covered with } AgCl).$$

In spite of the apparent differences between this and the cell last described, the two are entirely analogous. In the calculation of the electromotive force only the osmotic pressures of the silver ions in the nitrate solution and in the solution of the silver chloride require to be taken into account. The potassium chloride is used merely to increase the conductivity of the silver chloride solution. In practice a solution of potassium nitrate is inserted between the potassium chloride and silver nitrate solutions, in order to prevent the formation of a precipitate. The equation

$$\pi = \frac{0.0001983}{v} T \log \frac{P}{P_1}$$

holds good.

In the calculation of π the ratio $\frac{P}{P_1}$ alone need be known. The

value of v in this case is unity. In the nitrate solution the concentration of the silver ions may be known, if a solution of a certain strength be prepared; for if not very dilute, so that complete dissociation may be assumed, the degree of dissociation may be determined. In the case of the solution of silver chloride, the concentration of silver ions is not so easily ascertained. On account of the slight solubility of the chloride, it is certainly very small. By means of the electrical conductivity (page 137), the solubility in pure water may be determined. It has thus been found that the saturated silver chloride solution at 25° is 0.0000144 normal. In such a dilute solution the salt is doubtless practically all dissociated into the ions, $Ag^{\cdot}$ and Cl'; moreover, as they are present in equivalent amounts, the solution is 0.0000144 normal in respect to silver or chlorine ions, and the product of these concentrations is

$$Ag^{\cdot} \times Cl' = (0.0000144)^2 = S^2$$

when S represents the solubility of the salt.

Instead of a pure aqueous solution of silver chloride, that of the cell also contains potassium chloride. From page 202 it is seen that the product of the concentrations of the ions, divided by the concentration of the undissociated molecules, is a constant independent of the dilution, or,

$$\frac{C_{Ag^{\cdot}} \times C_{Cl'}}{C_{AgCl}} = K_d$$

and, since in a saturated solution the undissociated portion must be considered to remain constant, the same is true also of the product of the concentrations of the ions, or

$$C_{Ag^{\cdot}} \times C_{Cl'} = K.$$

When a relatively large amount of potassium chloride is added to a saturated aqueous silver chloride solution, the number of chlorine ions is greatly increased, and, in consequence, a certain amount of undissociated silver chloride must form and be precipitated, since the solution is already saturated with it. If C is the concentration of the silver ions after the addition, and also that of the chlorine ions derived from the silver chloride, while C_1 is the concentration of the added chlorine ions, then

$$C(C + C_1) = S^2,$$

and since C_1 is very great compared with C, the equation may be written

$$C = \frac{S^2}{C_1}.$$

To obtain the concentration of the ion corresponding to the material of the electrode, the square of the solubility S of the salt used is divided by the concentration of the other ion, of which an excess is added. Supposing a 0.1 normal potassium chloride solution to be used, C_1 for complete dissociation would be 0.1, but since at this concentration it is only about 85 per cent dissociated, $C_1 = 0.085$; and therefore

$$C = \frac{(0.0000144)^2}{0.085}.$$

Since the osmotic pressures are proportional to the concentrations, and the silver nitrate is 82 per cent dissociated, when the silver nitrate solution is 0.1 C_n, the following holds for 25° t: —

$$\pi = 0.000198 \times 298 \times \log \frac{0.082 \times 0.085}{(0.0000144)^2} = 0.44 \text{ volt.}$$

The corresponding value, experimentally determined by Goodwin, is 0.45 volt. The agreement is satisfactory.

The following arrangement is another example of such cells:[1] —

$$\begin{array}{l} Ag - KNO_3 \text{ sol., sat. with } AgBrO_3 \text{------} \\ Ag - KBrO_3 \text{ sol., sat. with } AgBrO_3 \text{------} \end{array}\Big|.$$

The concentration of the silver ions in the nitrate solution is nearly the same as in pure water, since the nitrate yields neither Ag nor BrO_3 ions, and consequently has but slight influence on the state of dissociation of the $AgBrO_3$. The concentration of the silver ions in the potassium bromate solution may be calculated as before, from the solubility of the silver bromate in water and the concentration of the BrO_3 ions added. When the values so obtained are substituted in the formula,

$$\pi = 0.0612 \text{ volt for } 0.1\ C_n,$$

and

$$\pi = 0.0454 \text{ volt for } 0.05\ C_n$$

solution of potassium bromate solution. The experimentally determined magnitudes are 0.0620 and 0.0471. The current, as before, passes through the cell from the weaker to the more concentrated solution of silver ions, *i.e.* from the bromate to the nitrate solution.

Electrodes in which the metal is in contact with one of its difficultly soluble salts, and also in the presence of a solution of a soluble salt with the same negative ion, were called by Nernst electrodes of the second order, or, as regards the negative ions, reversible elec-

[1] *Ztschr. phys. Chem.*, **13**, 577 (1894).

trodes. Ostwald showed that these are not to be distinguished from metal electrodes in a solution of one of their salts.

c. A third kind of concentration cell consists of those in which one of the electrolytes is a complex salt. As a type of this class, the following combination may be given: —

$$Ag - AgNO_3 \text{ sol.} - KCN \text{ sol. } (+ \text{ a little } AgCN) - Ag.$$

In the latter solution the complex salt $KAg(CN)_2$ is formed, the ions being $K^{\cdot}$ and $Ag(CN)_2'$. This negative ion is in turn dissociated to an extremely slight extent into $2(CN)'$ and $Ag^{\cdot}$, and it is the concentration of this latter silver ion which, in this solution, is to be taken into account in considering the electromotive force of the cell. It is evidently somewhat dependent upon the quantity of silver cyanide. Since it is at present impossible to measure the concentration of this small quantity of ions in the solution of the complex salt by an independent method, it is impossible to calculate the electromotive force of such cells. On the other hand, the measurement of the electromotive force gives a means of calculating the concentration. This is also true, naturally, of the cell previously described.

The calculation of the concentration from the measured electromotive force will now be carried out for the parallel case of the cell,[1]

$$\begin{array}{l} Hg - HgNO_3 \text{ solution, } 0.1\ C_n \text{----------} \\ Hg - Hg_2S \text{ dissolved in } Na_2S \text{ solution----} \end{array} \Big| .$$

The value of the electromotive force at 17° t was found to be 1.252 volts. Hence,

$$1.252 = 0.000198 \times 290 \log \frac{P}{P'},$$

where P and P' may represent either the osmotic pressures, or the concentrations of the mercury ions in the nitrate and sulfide solutions. Furthermore,

$$\log \frac{P}{P_1} = 21.8,$$

and

$$\frac{P}{P_1} = 10^{21.8}.$$

Assuming complete dissociation, there are 20 grams of mercury ions in a liter, or 1 mg. of ion in 0.00005 liter, of the 0.1 normal

[1] Behrend, *Ztschr. phys. Chem.*, 11, 466 (1893); see also *Ztschr. phys. Chem.*, 15, 495 (1894).

mercurous nitrate solution. This latter number, multiplied by 10^{n_s}, gives the number of liters of the sodium sulphide solution containing 1 milligram of mercury ions.

A means of determining the solubility of the difficultly soluble salts, and thereby the ion concentration, has already been found in the measurement of electrical conductivity. These considerations furnish, however, a second method far surpassing the first in delicacy. In fact, it is exactly at those extremely low concentrations, where all other methods are without avail, that the advantages of this one are most prominent, since the electromotive force becomes higher the greater the difference in the concentrations. In order to avoid error, however, what has been said on page 163 in regard to the capacity of the measuring instruments must be borne in mind.

Extrapolations such as the above[1] into the domain of extremely small ion concentrations are naturally accompanied with some uncertainty, since it is tacitly assumed that the regularities which have been found to exist in the case of ions of moderate concentration also exist in the case of ions of such small concentrations. Moreover, that the formation of potential and the activity of such cells can depend upon such slight concentrations of the metal ions is scarcely conceivable. It would seem necessary to ascribe an active part to the complex ions. Nevertheless, as will be shown in the section on the formation of potential at the electrodes, as long as it is assumed that the concentrations of the various substances, including the ions, are always related in a definite manner, and are in equilibrium with each other according to the law of mass action, the calculation of the potential is the same whichever the actual process taking place at the electrode may be. Bearing this in mind, it may be said that the measured values of the potentials correspond to the calculated small ion concentrations.

Attention may be called to the following important fact: In the three cells, —

1. Silver — $AgNO_3$ solution, 0.1 C_n | Silver — KCl solution, 0.1 C_n saturated with AgCl,
2. Silver — $AgNO_3$ solution, 0.1 C_n | Silver — KBr solution, 0.1 C_n saturated with AgBr,
3. Silver — $AgNO_3$ solution, 0.1 C_n | Silver — KI solution, 0.1 C_n saturated with AgI,

[1] See the discussion between Haber, Bödlander, Abegg, and Danneel, *Ztschr. Elektrochem.*, 10, 403, 604, 607, 609, and 773 (1904).

the electromotive force increases from the first to the third cell.

This is a consequence of the fact that the silver chloride is more soluble than the bromide, and this in turn more soluble than the iodide, and of the fact that all three salts are practically completely dissociated in their saturated solutions. In such cells as these the electromotive force is greater the less soluble the salt. With the complex instead of the insoluble salts, as is illustrated by the 0.1 normal potassium cyanide solution, to which some silver cyanide was added, the electromotive force is the greater the fewer the metal ions furnished by the salt (in this case silver). If a series of such cells be arranged in the order of their electromotive forces, beginning with the lowest, the order is also that of the solubility, or of the decomposition. Each salt in the series will dissolve in, and will react with, any of the saturated solutions of the cells following in the series. For example, silver chloride added to the potassium bromide solution forms silver bromide; silver bromide in the potassium iodide solution forms silver iodide, etc. When silver cyanide is added to a solution of sodium sulfide, it is changed into silver sulfide because the electromotive force of the cell,

$$\begin{array}{l} \text{Silver} - AgNO_3 \text{ solution, } 0.1\ C_n \text{----------} \\ \text{Silver} - Na_2S \text{ solution, } 0.1\ C_n \text{ saturated with } Ag_2S \text{---} \end{array},$$

is greater than that of the corresponding cyanide cell. On the other hand, silver sulfide does not dissolve in dilute potassium cyanide solution. The reason for this is easily seen when it is remembered that the more insoluble or complex a salt is, the lower is also the value of the product of the corresponding ions. If to a saturated silver chloride solution an amount of iodine ions (as in potassium iodide) be added equal to the chlorine ions present, silver iodide must precipitate; otherwise the product of concentration of the iodine and silver ions would be greater than its stable value. The concentration of the ions must, then, decrease in the only way possible, *i.e.* by the precipitation of solid silver iodide. This precipitation proceeds until the product of the ion concentrations has reached the constant value corresponding to the saturated silver iodide solution.

Such an arrangement of concentration cells is given in the following table:[1] —

[1] Ostwald, *Lehrb. der Allg. Chemie II*, 1, 882.

Silver Nitrate, 0.1 C_n against —	E, in Volts
Silver chloride, in potassium chloride of 1 C_n	0.51
Ammonia, 1 C_n	0.54
Silver bromide, in potassium bromide of 1 C_n	0.64
Sodium thiosulfate, 1 C_n	0.84
Silver iodide, in potassium iodide of 1 C_n	0.91
Potassium cyanide solution	1.31
Sodium sulfide, 1 C_n	1.36

A few drops of silver nitrate solution were added to the solutions of ammonia, sodium thiosulfate, and potassium cyanide, respectively.

Evidently the order of such a series may be changed by altering the concentrations of the electrolytes added to the silver salts. This might be done, for example, by adding a very concentrated solution of potassium chloride to the silver chloride solution; the concentration of the silver ions would thus be reduced below that of the 0.1 normal bromide solution, which contains silver bromide. In this case the electromotive force of the chloride cell would be greater than that of the bromide, and even if 0.1 normal potassium bromide solution be added to the chloride solution, silver bromide would not be precipitated; on the other hand, silver bromide could be dissolved in it. Similarly, silver sulphide would dissolve in concentrated potassium cyanide solution.

d. Finally, a concentration cell, which might also be included under description *a*, may be here considered, because of its peculiar characteristics. Attention was first called to it by Ostwald. A cell consisting of one hydrogen electrode in an acid solution, and another in an alkali solution, the two solutions being in contact, is a concentration cell with regard to hydrogen ions. It has already been learned that water is slightly dissociated into H and OH ions, and consequently a certain quantity of H ions is present in the alkali solution. The electromotive force of this cell is

$$\pi = \frac{RT}{\varepsilon} \ln \frac{P}{P_1},$$

P being the concentration or osmotic pressure of the hydrogen ions in the acid solution, and P_1 that of the ions in the alkali. Suppose the alkali and acid used to be normal solutions. The concentration P of the H ions in the acid solution, when the incomplete dissociation is taken into account, is about 0.8, and P_1 may be calculated from the measured electromotive force of the cell. In this case a considerable potential-difference exists at the surface of contact be-

tween the two solutions, which must be taken into consideration, since the sum of the potentials at the electrodes alone is desired. With the correction given by Nernst,[1] the value of π at 18° is 0.81 volt; that is,

$$0.81 = 0.0577 \log \frac{P}{P_1},$$

or

$$\frac{P}{P_1} = 10^{14.0}.$$

The concentrations of the hydrogen ions are proportional to their respective osmotic pressures. Then, since

$$C = 0.8,$$

the value of the concentration of the hydrogen ions in the alkali solution is as follows: —

$$C' = 0.8 \times 10^{-14}.$$

Now according to the law of mass action, the product of the hydrogen and hydroxyl ions must, in this case also, give a constant when divided by the concentration of the undissociated water, or,

$$\frac{C(\text{of } H') \times C(\text{of } OH')}{C(\text{of } H_2O)} = \text{const.}$$

The concentration of the undissociated water is so great in comparison with that of the ions, that it may be considered as a constant. Consequently, the product of the concentrations of the two ions must be a constant, or,

$$C(\text{of } H') \times C(\text{of } OH') = \text{const.}$$

But the concentration of the hydrogen ions in the alkali solution is

$$C' = 0.8 \times 10^{-14},$$

and that of the hydroxyl ions, according to the supposition, is

$$C = 0.8.$$

Hence

$$C' \times C = (0.8)^2 \times 10^{-14}.$$

From this result, the dissociation of water may be directly ascertained, for the product of the concentrations of the hydrogen and hydroxyl ions in pure water is the same as that of these ions in an alkali solution. Hence, for pure water,

$$C(\text{of } H') \times C(\text{of } OH') = (0.8)^2 \times 10^{-14}.$$

[1] *Ztschr. phys. Chem.*, 14, 155 (1894).

But, in this case, the concentration of the two ions is the same. Therefore, if C represents this concentration,

$$C^2 = (0.8)^2 \times 10^{-14},$$

or

$$C = 0.8 \times 10^{-7}.$$

In other words, pure water is 0.8×10^{-7} normal with respect to its hydrogen or hydroxyl ions. The conductivity measurements of Kohlrausch gave 0.75×10^{-7}. This is a very remarkable agreement, and its significance is made greater by the fact that other methods for reaching the same end, as through the study of the hydrolysis of salts and the saponifying effect of water, have led to very nearly the same value.

Oxygen electrodes may be used instead of hydrogen, and the cell still have the same electromotive force, because the concentrations of the hydrogen ions in the two solutions are in the same relation to each other as those of the corresponding hydroxyl ions. This follows from the fact that the product of the concentrations of the H and OH ions of the solutions in the cell is a constant. The fact that the platinum does not absorb oxygen as readily as it does hydrogen, and that it reaches a state of equilibrium with the surrounding gas more slowly, makes it more difficult to obtain constant results. In both cases, the current flows through the cell from the alkali to the acid solution.

It may be repeated here that, except for the potential-difference existing between the solutions at their point of contact, the electromotive force of such cells does not depend upon the nature of the negative ion of the acid, nor upon the positive ion of the alkali. On the other hand, when acids of the same molecular concentrations are used, the degree of dissociation comes into play. The cell

Hydrogen — Acetic acid solution----------¦
Hydrogen — Potassium hydroxide solution-------¦

would exhibit a lower electromotive force than the cell of corresponding concentrations,

Hydrogen — Hydrochloric acid solution----------¦
Hydrogen — Potassium hydroxide solution-------¦

The slightly dissociated acetic acid contains less hydrogen ions than the highly dissociated hydrochloric acid; consequently in the latter cell the difference in concentration between the hydrogen ions of the acid and alkali solutions is greater than in the former, and there-

fore its electromotive force is also greater. That the same considerations apply to bases may be safely concluded from the measurements which have already been made in that direction.

3. **Concentration Double-Cells.** — Another kind of concentration cell may be formed by combining two simple cells into a double-cell. The so-called calomel cell, which is very often used, serves as a type of such a double-cell. Its combination is as follows: —

$$\begin{array}{l} Zn - ZnCl_2 \text{ solution, conc.} \\ \qquad Hg \begin{cases} HgCl \text{ solution, sat.} \\ HgCl \text{ solution, sat.} \end{cases} \\ Zn - ZnCl_2 \text{ solution, dil.} \end{array}$$

The mercurous chloride is in excess, and covers the mercury. This cell differs from the simple cell,

$$Zn - ZnCl_2 \text{ solution, conc.} - ZnCl_2 \text{ solution, dil.} - Zn,$$

in having the combination, —

$$HgCl - Hg - HgCl,$$

between its two differently concentrated solutions of zinc chloride. Consequently, the processes of electrolysis and the electromotive forces of such double-cells differ from those of the simpler cells. In the case of the simple cell, when $2\underline{Q}$ coulombs of electricity pass, there is a migration of zinc and chlorine ions from one solution to the other, and a simultaneous solution and precipitation of two equivalents of zinc at the electrodes. In the calomel concentration cell such a migration cannot occur. When $2\,\underline{Q}$ coulombs pass through this cell, two equivalents of zinc dissolve in the dilute chloride solution, and two of mercury separate from the mercurous chloride. Here the current always passes from the dilute to the concentrated solution within the cell. The mercury ions come from the dissolved mercurous chloride, and those precipitated are immediately replaced by the further solution of mercurous chloride. In the concentrated solution, on the other hand, two equivalents of zinc separate at the electrode, and two of mercury are dissolved. It must be borne in mind that when two equivalents of metallic mercury have been produced from the solid mercurous chloride in the dilute solution, two equivalents of chlorine ions have also been formed; and when two equivalents of metallic mercury have changed to mercurous chloride in the concentrated solution at the same time, two of chlorine ions have disappeared. When the quantities of the solutions are imag-

ined so great that these changes take place without sensible influence on the concentration, the processes may be summarized as follows: Two equivalents of zinc and two of chlorine — that is, one mol of zinc chloride — have been transferred from the concentrated solution to the dilute, while the quantity of mercury and of mercurous chloride remains unaltered. If the osmotic pressure of the zinc ions in the concentrated solution be P, and in the dilute solution P_1, then the corresponding osmotic pressures of the chlorine ions are $2P$ and $2P_1$. The maximum osmotic work is easily calculated, and is given by the equation,

$$W_\infty = RT \ln \frac{P}{P_1} + 2RT \ln \frac{2P}{2P_1} = 3RT \ln \frac{P}{P_1}.$$

The electrical energy is $2 \mathrm{E} \mathfrak{Q}$, therefore

$$\mathrm{E} = \frac{3}{2} \frac{RT}{2\mathfrak{Q}} \ln \frac{P}{P_1}.$$

In general,

$$\mathrm{E} = \frac{n_i}{\nu} \frac{RT}{\mathfrak{Q}} \ln \frac{P}{P_1},$$

where n_i is the number of ions formed from one molecule of the electrolyte, and ν the number of electrochemical units $\mathfrak{Q}$ required to transfer one mol of the electrolyte from the concentrated to the dilute solution. It is evident from a comparison of this equation with that given on page 199 that here we have another method for the calculation of the transference numbers of an electrolyte.

From the formula it may be seen that only the ratio $\frac{P}{P_1}$, n_i, and ν have influence on the value of the electromotive force E. As Ostwald predicted, and as Goodwin[1] experimentally demonstrated, it follows that: —

1. The mercurous chloride and mercury of the calomel cell may be replaced by silver chloride and silver without altering the electromotive force.

2. Instead of zinc chloride, zinc bromide or iodide may be used when the depolarizer[2] is a difficultly soluble bromide or iodide, without changing the electromotive force.

3. The electromotive force of the cell will not be changed if cadmium chloride and cadmium be substituted for zinc chloride and zinc.

[1] *Ztschr. phys. Chem.*, **13**, 577 (1894).

[2] The difficultly soluble salt is here called a depolarizer, because, through its presence, the electrode is made unpolarizable for small currents.

4. If the zinc and zinc chloride be replaced by thallium and thallium chloride, the electromotive force will be considerably increased.

5. If instead of the chloride of zinc, the sulfate be used, with a difficultly soluble sulfate as depolarizer, the electromotive force will be less than before. Whether lead or mercurous sulfate be used as depolarizer can make no difference. The accompanying tables confirm these statements. For the sake of brevity the cells are designated by their soluble salts and depolarizers.

I

$ZnCl_2$ — HgCl and $ZnCl_2$ — AgCl Cells at 25°

Concentration of the $ZnCl_2$	Observed E. M. F. of $ZnCl_2$ – HgCl	Observed E. M. F. of $ZnCl_2$ – AgCl	Calculated E. M. F. in Volts
0.2 – 0.01	0.0787	0.0767	0.0797
0.1 – 0.01	0.0800	0.0780	0.0818
0.02 – 0.002	0.0843	0.0843	0.0844
0.01 – 0.001	0.0861	0.0847	0.0853

Considering the experimental errors of 1 to 2 thousandths of a volt, the agreement is very satisfactory.

II

$ZnBr_2$ — HgBr and $ZnBr_2$ — AgBr Cells

Concentration of the $ZnBr_2$	Observed E. M. F. of $ZnBr_2$ – HgBr	Observed E. M. F. of $ZnBr_2$ – AgBr	Calculated E. M. F. in Volts
0.2 – 0.02	0.0793	0.0793	0.0797
0.1 – 0.01	0.0808	0.0802	0.0818
0.02 – 0.002	0.0860	0.0852	0.0852
0.01 – 0.001	0.0863	0.0858	0.0853

Through replacement of zinc and its chloride by cadmium and cadmium chloride, the value of the electromotive force could not be calculated, the concentration of the cadmium ions not being determinable with exactness (by the conductivity method). This is explained by the fact that $CdCl_2$ dissociates not only into $Cd^{\cdot\cdot}$ and Cl', Cl', but probably also, in concentrated solutions, into $CdCl^{\cdot}$ and Cl'. In dilute solutions, where only the former dissociation is considerable, the values calculated agree with those experimentally found.

III

TlCl — HgCl Cells

Concentration of the TlCl	Observed E. M. F.	Calculated E. M. F.
0.0161 — 0.00161	0.102	0.114
0.008 — 0.0008	0.100	0.115
0.0161 — 0.008	0.0328	0.033

The experimental errors in this case are greater than those in the two previous tables.

IV

$ZnSO_4$ — $PbSO_4$ Cells

Concentration of the $ZnSO_4$	Observed E. M. F.	Calculated E. M. F.
0.2 — 0.02	0.0427	0.0453
0.1 — 0.001	0.0440	0.0471
0.02 — 0.002	0.0522	0.0500

V

$ZnSO_4$ — Hg_2SO_4 Cells

Concentration of the $ZnSO_4$	Observed E. M. F.	Calculated E. M. F.
0.2 — 0.02	0.047 — 0.034	0.045
0.1 — 0.01	0.045 — 0.033	0.047

The formula $$E = \frac{n_i}{\nu}\frac{RT}{Q}\ln\frac{P}{P_1}$$

is only applicable when the solubility of the depolarizer is inappreciable. If, for example, the difficultly soluble mercurous chloride of the calomel cell be replaced by the comparatively easily soluble thallium chloride, it must be taken into account that the concentrations of the zinc and the chlorine ions are no longer in the same relation. Chlorine ions from the thallium chloride are thus added to

those of the zinc chloride, and from the law of mass action the product of the ion concentrations of the thallium and chlorine in the saturated thallium chloride solution is constant, and more chlorine ions must enter the dilute than the concentrated zinc chloride solution. From this consideration, taking into account the previous deduction, P and P_1 being the osmotic pressures or the concentrations of the zinc ions, and P' and P_1' those of the chlorine ions,

$$2\,\text{E}\mathfrak{Q} = RT\ln\frac{P}{P_1} + 2\,RT\ln\frac{P'}{P_1'};$$

$$\text{E} = \frac{RT}{\mathfrak{Q}}\left(\frac{1}{2}\ln\frac{P}{P_1} + \ln\frac{P'}{P_1'}\right). \qquad (1)$$

In general, $$\text{v}\text{E}\mathfrak{Q} = n_i RT\ln\frac{P}{P_1} + n_i'\,RT\ln\frac{P'}{P_1'},$$

where n_i and n_i' represent the number of cations and anions which the molecule of the electrolyte produces, and v the number of $\mathfrak{Q}$ units corresponding to the transference of one molecule of the electrolyte from the concentrated to the dilute solution.

The electromotive force of the cell may also be calculated from the electrolytic solution pressures of the two metals coming into consideration (in the calomel cell, the zinc and mercury). In this case the electromotive force of the cell consists of four potential-differences, existing at the four points of contact between metal and liquid. If P_{Zn} and P_{Hg} represent the solution pressures of the zinc and mercury respectively, and P, P_1, P', and P_1' the concentrations of the zinc and mercury ions in the concentrated and in the dilute solutions, while v_{Zn} and v_{Hg} are the valencies of the metals, then taking into consideration the fact that the current passes through the cell from the dilute to the concentrated solution, the electromotive force is represented by the following equation: —

$$\text{E} = \frac{RT}{\mathfrak{Q}}\left(\frac{1}{\text{v}_{\text{Zn}}}\ln\frac{\text{P}_{\text{Zn}}}{P_1} + \frac{1}{\text{v}_{\text{Hg}}}\ln\frac{P_1'}{\text{P}_{\text{Hg}}} + \frac{1}{\text{v}_{\text{Hg}}}\ln\frac{\text{P}_{\text{Hg}}}{P'} + \frac{1}{\text{v}_{\text{Zn}}}\ln\frac{P}{\text{P}_{\text{Zn}}}\right).$$

This may be shortened to the form

$$\text{E} = \frac{RT}{\mathfrak{Q}}\left(\frac{1}{\text{v}_{\text{Zn}}}\log\frac{P}{P_1} + \frac{1}{\text{v}_{\text{Hg}}}\log\frac{P_1'}{P'}\right),$$

or $$\text{E} = \frac{RT}{\mathfrak{Q}}\left(\frac{1}{2}\ln\frac{P}{P_1} + \ln\frac{P_1'}{P'}\right). \qquad (2)$$

Equations (1) and (2) lead to the same result, in spite of their

apparent difference. In (1) $\frac{P'}{P_1'}$ represents the concentration relation of all the negative ions of the solutions, while in (2) $\frac{P_1'}{P'}$ represents that of the cations of the depolarizer. It must be remembered that saturated solutions of the depolarizer are being considered; consequently the product of the concentrations of all the anions and cations of the depolarizer is a constant (the anions of the electrolyte and depolarizer being always alike, as in the case of $ZnCl_2$ and HgCl). The separate concentrations are also in a definite relation to each other. When, for instance, the cations and anions are of the same valency, as in the example, their different concentrations in the solutions are inversely proportional to each other. If the anion be bivalent and the cation univalent, the concentration of the latter is inversely proportional to the square of that of the former, and so on. This explains the agreement of the two equations.

Use of the Electrometer as an Indicator in Titration. — After the explanation of the above concentration cells, the interesting use of the electrometer as an indicator will be easily understood. In order to illustrate this application, consider the concentration cell

$$Ag - AgNO_3 \text{ sol., } 0.1\ C_n - AgNO_3 \text{ sol., } 0.1\ C_n - Ag,$$

the electromotive force of which is equal to zero. If to one of the two solutions potassium chloride is added, the difficultly soluble precipitate, silver chloride, is formed, the concentration of the silver ions is decreased, and an electromotive force is produced in the cell. As more potassium chloride is added, the electromotive force of the cell increases, at first slowly, then faster and faster until a sudden change takes place, and then slowly again. This behavior may be at once understood from a consideration of the equation,

$$E = 0.0575 \log \frac{P}{P'},$$

in which P and P' represent the two concentrations of the silver ions. If, for example, while P is maintained constant the value of P' is decreased to one hundredth of its original value, the electromotive force becomes

$$E = 2 \times 0.0575 \text{ volt.}$$

In order to produce this decrease in concentration, it would be necessary to add to 1000 cubic centimeters of the 0.1 normal solution of silver nitrate about 980 cubic centimeters of a 0.1 normal solution of potassium chloride, if both solutions are completely dis-

sociated. The new value of P' may be decreased to one hundredth of its value by the further addition of 19.8 cubic centimeters, and the value of P' so obtained may be decreased to the same extent by the addition of 0.198 cubic centimeter of 0.1 normal potassium chloride solution, etc. With each successive decrease in the value of P', the electromotive force of the cell is increased by 2×0.0575 volt. As follows from what has just been stated, the greatest change of the electromotive force with the addition of the potassium chloride solution occurs when the last portion of silver nitrate disappears, or, better expressed, when the concentrations of the silver and of the chlorine ions are nearly equal. The increase of the electromotive force with further additions of potassium chloride is very slight, being due to the decrease of the silver ions by the mass-action effect of the added chlorine ions. When the original concentration of the silver is known, this method may also be used for the determination of the halogens.[1] With the aid of two hydrogen electrodes it may be used in acid and alkali titrations.[2]

LIQUID CELLS

It has already been stated in the consideration of the concentration cells that potential-differences occur at the points of contact between the solutions. This assumption has been entertained a long time, but a clear conception of the origin of such potentials did not exist. The Becquerel acid-alkali cell is well known; two platinum electrodes connected together are placed one into acid and the other into alkali solution. That in the acid becomes positively, and the other negatively, charged; the potential-difference, varying with the conditions, often amounts to more than 0.6 volt. Formerly the source of this electrical energy was erroneously thought to be in the heat generated by the neutralization of the acid and alkali. As previously explained, this is practically a concentration cell. Oxygen of the air is present at the two electrodes, and in the acid solution there are few, while in the alkali there are many, OH ions. Since the electrodes are of ordinary platinum instead of being coated with platinum black, it is easily explicable that the electromotive force of such a cell is variable. Ordinary platinum does not absorb oxygen to a very great extent, so that the condition of equilibrium which should be established, in which the concentration of the oxygen dissolved in the platinum corresponds

[1] *Ztschr. phys. Chem.*, 11, 466 (1893).
[2] *Ztschr. phys. Chem.*, 24, 253 (1897).

to the pressure of the surrounding oxygen, as in the case of platinized platinum, is practically unrealizable; consequently the cell has an uncertain and varying value. This cell cannot generate a perceptible current, because the quantity of oxygen absorbed by the electrodes is very small, and, being exhausted, is replaced by that of the air only very slowly. The presence of other gases, such as hydrogen, also has an influence upon the electromotive force of this cell.

We are indebted to Nernst[1] for satisfactory explanations of the phenomena of these liquid cells, their theory having been developed by him. If a solution of hydrochloric acid, for example, be placed in contact with a more dilute solution or with pure water, the acid will diffuse into the water. The hydrogen and chlorine ions of the acid are, to a certain extent, independent particles capable of moving with different velocities from places of higher osmotic pressure to those of lower. Since the hydrogen ions migrate more rapidly than those of chlorine, the foremost of the diffusing ions are hydrogen, and since these possess positive charges, the water or the dilute solution as a whole exhibits a positive, and the stronger solution a negative, charge. Owing to the mutual attraction of the positive and negative charges of the hydrogen and chlorine ions, this separating process does not actually take place to any measurable extent, the hydrogen ions are delayed, and the chlorine ions increase their speed, so that a condition is reached in which both migrate at the same rate. The electrostatic attraction, as well as the potential difference between the solutions, exists until both solutions are homogeneous.

The unequal velocities of migration of the ions are therefore the cause of the potential-differences at the contact surfaces of differently concentrated solutions,

If the negative ions have the greater velocity of migration, the more dilute solution will evidently be negative to the concentrated. In other words, *the dilute solution always presents the electricity of the more rapidly moving ion.*

Moreover, it is thus not only possible to foresee the nature of the potential-difference at the point of contact between two liquids, but also in many cases quantitatively to calculate the magnitude of such potential-differences, and to prove the calculations by actual experiment. To illustrate this point, two differently concentrated solutions of an electrolyte, consisting of two univalent ions, may be imagined in contact. Let $(1 - n_a)$ be the share of the transport

[1] *Ztschr. phys. Chem.*, 4, 129 (1889).

of the positive ion, and consequently n_a that of the negative. The quantity of electricity ϱ is now conducted *through the solutions from the concentrated to the dilute*, then $(1 - n_a)$ positive gram-ions pass from the concentrated into the dilute, and at the same time n_a negative gram-ions from the dilute into the concentrated solution. Let P represent the concentration of the positive and negative ions in the concentrated solution, and P_1 the same in the dilute solution. The maximum work, the process being completed osmotically, is

$$W = (1 - n_a)\, RT \ln \frac{P}{P_1} - n_a\, RT \ln \frac{P}{P_1},$$

or

$$W = (1 - 2n_a)\, RT \ln \frac{P}{P_1},$$

or if n_a be replaced by $\frac{v_a}{v_c + v_a}$, v_c being the velocity of migration of the positive, and v_a that of the negative, ions,

$$W = \frac{v_c - v_a}{v_c + v_a}\, RT \ln \frac{P}{P_1}.$$

Consequently

$$\mathrm{E} = \frac{v_c - v_a}{v_c + v_a} \frac{RT}{\varrho} \ln \frac{P}{P_1}, \qquad (a)$$

because

$$\mathrm{E}\varrho = W.$$

If v_c be greater than v_a, the electric current passes from the concentrated to the dilute solution in the cell itself; if v_a be greater than v_c, the current passes in the opposite direction. If, finally, $v_c = v_a$, no potential-difference exists between the solutions, and consequently there is no current.

Nernst constructed such liquid cells so that the potential observed was only that appearing at the point of contact of two solutions, and compared the experimentally determined values of the electromotive force with those calculated from the equation derived above. The following arrangement was used:—

Hg — KCl solution, 0.1 C_n, sat. with HgCl ------ 1
2 ---------- KCl, 0.01 C_n ----------
---------- HCl, 0.01 C_n ---------- 3
4 ---------- HCl, 0.1 C_n ----------
------ KCl solution, 0.1 C_n, sat. with HgCl — Hg.

Since the two ends are identical, the potential-differences occurring there neutralize each other, and therefore only those differences at the four contact points 1, 2, 3, and 4 are to be taken into account.

It is to be observed that, as far as experience has gone, the rule holds also for liquid cells that *only the ratio, not the absolute values of the osmotic pressures, comes into consideration.* (Nernst's principle of superposition. Each system may be imagined to be formed from the others by means of n-fold superposition.) Therefore the potential-difference of 2 is equal and oppositely directed to that of 4. Thus the potential-differences at 1 and 3 alone remain, and may be calculated from the above formula. If u'_c and u'_a are the velocities of migration of the potassium and chlorine ions respectively, while u''_c and u''_a ($= u'_a$ because the negative ions are the same) are the migration velocities of the hydrogen and chlorine ions, then the sum of the potential-differences is represented by

$$\pi = \frac{u'_c - u'_a}{u'_c + u'_a} \frac{RT}{\varepsilon} \ln \frac{P}{P_1} \frac{u''_c - u''_a}{u''_c + u''_a} \frac{RT}{\varepsilon} \ln \frac{P'}{P_1'},$$

and as

$$\frac{P}{P_1} = \frac{P'}{P_1'},$$

therefore

$$\pi = \left(\frac{u'_c - u'_a}{u'_c + u'_a} - \frac{u''_c - u''_a}{u''_c + u''_a} \right) \frac{RT}{\varepsilon} \ln \frac{P}{P_1}.$$

P and P_1 are the osmotic pressures or concentrations of the potassium and chlorine ions in the concentrated and dilute potassium chloride solutions, P' and P_1' the corresponding values of the hydrogen and chlorine ions in the corresponding hydrochloric acid solutions. The actual measured potential-difference was -0.0357 volt. The negative sign is used, since the current in the cell flows in the direction 4 to 1, and since, in the calculation, it has been considered positive when it passed from the concentrated to the dilute potassium chloride solution. The potential-difference resulting from calculation by the formula, taking into consideration the incomplete dissociation of the substances, differs from the above by about four to five per cent.

The equation (a) only permits of calculation of the potential-difference at the points of contact of two differently concentrated solutions of one and the same binary electrolyte. If it is desired to make it applicable to electrolytes whose ions have different valencies, it takes the form

$$\pi = \frac{\frac{u_c}{v} - \frac{u_a}{v'}}{u_c + u_a} \frac{RT}{\varepsilon} \ln \frac{P}{P_1}, \qquad (b)$$

v representing the valence of the positive and v' that of the negative ion.

If two different electrolytes are in contact, as, for instance, potassium chloride and hydrochloric acid, the calculation is more difficult. Only for the case in which the total concentration of ions in each of the two solutions is the same, the following simple expression holds:—

$$\pi = \frac{RT}{\varrho} \ln \frac{u'_c + u''_a}{u''_c + u'_a}, \qquad (c)$$

where u'_c and u'_a are the migration rates of the ions of one electrolyte, u''_c and u''_a those of the other. The electromotive force is here independent of the ratio of the concentrations.

The calculation is still more difficult when one of the electrolytes contains polyvalent ions. If all the ions of the two solutions of binary electrolytes are polyvalent and of the same valency, then when the ion concentrations are the same,

$$\pi = \frac{RT}{v\varrho} \ln \frac{u'_c + u''_a}{u''_c + u'_a}. \qquad (d)$$

It is worthy of special attention that in general there can be no arrangement of solutions in an electromotive series such as Volta formed for the metals. This is evident from the fact, already mentioned, that such solution cells as the one measured by Nernst (see pages 219 and 220) produce a current. A circuit consisting of metals only, at a common temperature, does not generate an electric current. If, on the other hand, the solutions of the above cell, without the mercury and the mercurous chloride, be arranged in a circuit as shown in Figure 45, an electric current is obtained whose electromotive force is that previously calculated. The existence of this current may be demonstrated by its power of induction, and it lasts until the concentration of the various ions is the same throughout the system.

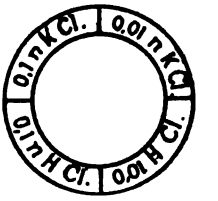


FIG. 45

The law of electromotive series applies only to differently concentrated solutions of the same electrolyte in juxtaposition. That it holds in this case may be shown by adding the potential-differences occurring at the different points of contact, and comparing the sum with the potential-difference actually observed between the first and last solutions placed directly in contact. The intermediate members of the series are thus shown to play no part.

In considering concentration cells, such conditions were usually chosen that the potential-differences occurring at the contact points

of the solutions were negligible.[1] Under such circumstances the electromotive force as previously given, for a cell in which the metal electrodes dip into the two differently concentrated solutions of the salt, is

$$\text{E} = \frac{RT}{\nu\varrho} \ln \frac{P}{P_1}.$$

This equation was obtained by adding the potential-differences existing at the electrodes — that is, with the application of the idea of electrolytic solution pressure. In the addition the solution pressures were cancelled from the equation, as they have the same value for the two similar electrodes and are oppositely directed.

It was also found possible to obtain the value of E, without any assumption of solution pressure, by the so-called purely energetic method. It was only necessary to take into account the condition of the system before and after the passage of a certain quantity of electricity, without attempting to understand why a potential-difference and electric current are manifested. The maximum work obtainable osmotically by the change of the system from its original to its ultimate state is calculated, and this maximum is considered as the equivalent of the electrical energy obtainable from the process. The values of E calculated in both ways agreed without exception.

It remains to be seen whether, when a potential-difference occurs at the point of contact of the liquids, the two methods of calculation still yield the same result. For this purpose, the following concentration cell is selected: —

Zinc — $ZnCl_2$ solution, concentrated
Zinc — $ZnCl_2$ solution, dilute.

1. *Calculation of* E *by means of the electrolytic solution pressure.*

The electromotive force of the cell consists of three potential-differences, namely, the two at the electrodes and that at the point of contact between the two liquids. The sum of the first two is

$$\text{E}_1 + \text{E}_2 = \text{E}_{(1+2)} = \frac{RT}{2\varrho} \ln \frac{P}{P_1},$$

where P and P_1 are the osmotic pressures of the zinc ions in the concentrated and dilute solutions, respectively, the corresponding pressures of the chlorine ions being $2P$ and $2P_1$.

[1] For a description of a means for attaining this end, see *Ztschr. phys. Chem.*, **14**, 145 (1897).

The third potential-difference is calculated according to the formula (*b*), and is

$$\pi_3 = \frac{\frac{u_c}{2} - \frac{u_c}{1}}{u_c + u_a} \frac{RT}{\varrho} \ln \frac{P}{P_1},$$

where u_c and u_a are the velocities of migration of the zinc and chlorine ions. The sum of $\pi_{(1+2)}$ and π_3 is

$$\pi_{(1+2+3)} = \frac{RT}{\varrho} \ln \frac{P}{P_1} \left(\frac{1}{2} - \frac{u_c - 2u_a}{2(u_c + u_a)} \right) = \frac{3u_a}{2(u_c + u_a)} \frac{RT}{\varrho} \ln \frac{P}{P_1},$$

or if the transportation ratios are introduced, $n_a = \frac{u_a}{u_c + u_a}$

and $1 - n_a = \frac{u_c}{u_c + u_a}$,

and $$\pi_{(1+2+3)} = \frac{3n_a}{2\varrho} RT \ln \frac{P}{P_1}.$$

π_3 must be subtracted from $\pi_{(1+2)}$ as indicated, since the calculation of π_3 presupposes the direction of the positive current from the concentrated to the dilute solution within the cell, while with $\pi_{(1+2)}$ the current passes in the opposite direction.

2. *Calculation of* π *by means of the principles of energetics.* The process is exactly that outlined on page 198. If 2ϱ be allowed to pass through the cell, an ion-mol of zinc passes into the dilute, while the same quantity is deposited from the concentrated, solution. In addition, the quantity $(1 - n_a)$ ion-mols of zinc passes from the dilute to the concentrated solution, $(1 - n_a)$ being the transference share of the zinc ions. The dilute solution is now richer by n_a ion-mols of zinc, while the concentrated one has lost this amount. Simultaneously, however, an amount of chlorine ions equivalent to the n_a zinc ions has also passed from the concentrated to the dilute solution; consequently the quantity n_a ion-mols of zinc and its equivalent of chlorine ions have been moved from the concentrated to the dilute solution. The maximum osmotic work corresponding to the zinc ions is

$$W' = n_a RT \ln \frac{P}{P_1},$$

and since there are two chlorine ions to each zinc ion, it has for the chlorine ions the value

$$W'' = 2n_a RT \ln \frac{P}{P_1},$$

or, added together, $$W = 3n_a RT \ln \frac{P}{P_1}.$$

The electrical energy is $2\,\mathrm{F}\underline{\varrho}$, and therefore

$$\mathrm{F} = \frac{3\,n_s}{2\underline{\varrho}} RT \ln \frac{P}{P_1},$$

which is the same as the equation derived above.

This agreement in the methods gives also a method for determining the magnitude of potential-differences at the contact points of liquids. It is only necessary to calculate, as above, the sum of the potential-differences occurring at the two electrodes, and subtract it from the actually measured electromotive force of the whole cell, to obtain the desired value.

Finally, it should also be mentioned that the electromotive force of concentration cells may also be calculated by means of an application of the principles of energetics to processes other than the osmotic process used in this book. For instance, the process of isothermal distillation, first used by Helmholtz,[1] is well adapted to the calculation of the electromotive forces of concentration cells. In making use of this process, a knowledge of the vapor pressures of the differently concentrated solutions is essential.

On the whole, the process involving osmotic pressures is to be preferred in the case of dilute solutions because the requisite knowledge of the osmotic pressure, or the proportional concentration of the ions, is readily available.

GENERAL CONSIDERATION OF CONCENTRATION AND LIQUID CELLS

All the cells thus far described have the common characteristic that *their electrical energy is not generated from chemical energy.* In every case there was simply a passage of material from a higher to a lower pressure, and whether it be gas or a dissolved substance which undergoes this change, the process does not affect the internal energy. The work done does not therefore come from the internal energy, but is derived from the heat of the surroundings. Consequently *the galvanic cells thus far considered are really machines for transforming the heat of their surroundings into electrical energy.*

According to the generally applicable formula of Helmholtz (see page 173),

$$\mathrm{F}\underline{\varrho} - Q = \underline{\varrho} T \frac{d\mathrm{F}}{dT}.$$

[1] *Wied. Ann.*, **3**, 201 (1878), and **14**, 61 (1881).

In the present case Q, the heat generated by the chemical reaction, is zero; therefore

$$\mathfrak{F}\mathfrak{Q} = \mathfrak{Q}T\frac{d\mathfrak{F}}{dT}; \text{ or } \frac{\mathfrak{F}}{T} = \frac{d\mathfrak{F}}{dT}; \text{ and } \mathfrak{F} = T\frac{d\mathfrak{F}}{dT}.$$

This, on integration, gives

$$\ln \mathfrak{F} = \ln T + k \text{ or } \frac{\mathfrak{F}}{T} = k.$$

The change of the electromotive force of these cells with the temperature is determined by the relation existing between the electromotive force and the corresponding absolute temperature. The electromotive force itself is proportional to the absolute temperature. When in activity, the cell cools itself and takes up heat from the surroundings.

The same conclusions are reached on proceeding in still another way. The electromotive force of one of the previously mentioned concentration or liquid cells is, in general,

$$\mathfrak{F} = x\frac{RT}{\mathfrak{Q}}\ln\frac{P}{P_1}, \qquad (a)$$

from which

$$\frac{\mathfrak{F}}{T} = x\frac{R}{\mathfrak{Q}}\ln\frac{P}{P_1}. \qquad (b)$$

On differentiation with respect to T

$$\frac{d\mathfrak{F}}{dT} = x\frac{R}{\mathfrak{Q}}\ln\frac{P}{P_1} \qquad (c)$$

is obtained, if x and $\ln\frac{P}{P_1}$ for "ideal" solutions are considered as practically independent of the temperature.

By combination of (b) and (c),

$$\frac{\mathfrak{F}}{T} = \frac{d\mathfrak{F}}{dT}$$

is again obtained.

It will be well to bear in mind that the electromotive force is only correctly calculable by this method when the solutions are so dilute that the laws of gases are applicable, for it is upon this assumption that the maximum work is estimated. As a matter of fact solutions are often used which, on being mixed, generate considerable quantities of heat, and are therefore far from being ideal solutions. For

such solutions the Q of Helmholtz's formula is evidently not zero, and the relation,

$$\frac{E}{T} = \frac{dE}{dT}$$

no longer holds good.

It is, then, to be noticed that the Helmholtz equation in its above form applies only when the chemical process resulting from the passage of a definite quantity of electricity is not a function of the temperature. This is, however, not the case for most concentration or liquid cells, since the transference number n_a, and, among other properties, also the valence v, is a function of the temperature. For this reason, the quantity x which appears in the second equation derived cannot be considered as independent of the temperature. In agreement with these considerations it is found that the electromotive force of such cells in general is not at all proportional to the absolute temperature.

In still another respect the application of the Helmholtz equation is of interest. Generally the electromotive force of a cell cannot, as has often been emphasized, be calculated from the value of its heat effect alone. In the following case, however, the electromotive force can be so calculated, or, more strictly speaking, the value of

$$\frac{dE}{dT},$$

which, together with the value of Q, must be known in order to calculate E, may, in the case of many concentration cells, be calculated directly from the value of Q. This has been shown by van't Hoff, Cohen, and Bredig.[1]

Consider the concentration cell,

$$\begin{array}{l} Hg,\ Hg_2SO_4,\ \text{solid},\ -\ Na_2SO_4,\ \text{saturated} \\ Hg,\ Hg_2SO_4,\ \text{solid}\ -\ Na_2SO_4,\ 0.25\ C_a \end{array}$$

It is evident that the electromotive force of this cell will be equal to zero at the temperature at which the saturated solution of sodium sulfate is 0.25 normal. If at this temperature, which is $-16.2°\ t$, a current be allowed to pass through the cell, sodium sulfate goes

[1] *Ztschr. phys. Chem.*, **16**, 453 (1895). As has been mentioned by Nernst, here also the modified Helmholtz equation,

$$\frac{Qd\varepsilon}{dT} - \frac{Q\varepsilon dn_a}{n_a dT} = \frac{\varepsilon Q - Q}{T},$$

must be used because of the variability of n_a.

into solution on one side and separates on the other. The value of Q is easily calculated from the heats of solution and dilution of the salt. The following form of the Helmholtz equation may now be applied: —

$$\left(\frac{d\pi}{dT}\right)_{t=-16.2^\circ} = -\frac{Q}{T}.$$

If this value of $\frac{d\pi}{dT}$ be multiplied by 16.2°, the preliminary value of π at 0° t is obtained. With the aid of this value and the exact value of Q at 0° t, the value of

$$\left(\frac{d\pi}{dT}\right)_{t=0^\circ}$$

may be calculated. If, further, the average of the two values

$$\left(\frac{d\pi}{dT}\right)_{t=-16.2^\circ} \text{ and } \left(\frac{d\pi}{dT}\right)_{t=0^\circ}$$

be multiplied by 16.2, a more accurate value of π at zero is obtained. By a repetition of this calculation the value of π at 0° t becomes more and more nearly correct. The value of the electromotive force obtained experimentally agrees well with the value calculated in this manner.

It is especially evident from this example that it is not in harmony with fact to consider the heat of solution, or of dilution, etc., exclusively as the source of the electrical energy, for, at −16.2° for example, the heat of solution of sodium sulfate is very great, while the electrical energy is equal to zero. On the other hand, there is a close relation between the temperature coefficient of the electromotive force and the heat of solution. This appears accountable when it is considered that the heat of solution is closely related to the temperature coefficient of the logarithm of the concentration, and that the electromotive force depends upon the latter value.

In the concentration cell,

Hydrogen in platinum black — alkali solution ------,
Hydrogen in platinum black — acid solution --------'

the electromotive force depends principally upon the difference between the concentrations of the hydrogen ions in the two solutions. When the cell is in operation, the neutralization of acid and base takes place, not at the point of contact of the two solutions, but at the electrodes. The electromotive force of this cell can be calculated

from the heat effect of the process, *i.e.* the heat of neutralization, only with the aid of its temperature coefficient.

THERMOELECTRIC CELLS—THE ELECTROMOTIVE SERIES

In connection with the foregoing a few words may well be devoted to thermoelectric cells. Heat is here subjected to a transformation into electrical energy caused by a difference of temperature. On the other hand, in the concentration cells heat at a constant temperature is changed into electricity, accompanied by the simultaneous passage of a substance from a higher to a lower concentration. This cannot be considered as contrary to the second law of thermodynamics, because, according to this law, it is only in a *cyclical process* that no heat at constant temperature can be changed into work. In other processes such a transformation may well occur.

The potential-difference at one electrode may be expressed by the equation,

$$\pi = \frac{RT}{\nu \varrho} \ln \frac{p}{P},$$

and is accordingly proportional to the absolute temperature. The arrangement

$$Zn - ZnSO_4 \text{ solution}, - Zn$$

will produce no electrical energy at constant temperature, since the two potential-differences of such a cell are equal and oppositely directed. But if one of the contact points between electrode and solution be warmed, the corresponding potential-difference changes and an electric current is produced. As the potential-difference at the point of contact between two solutions is also proportional to the absolute temperature, it is immediately clear that the following cyclical arrangement should produce an electric current:

$$\begin{array}{l} \text{Solution } C_1 \text{ at } T_1 - \text{Solution } C_2 \text{ at } T_1 \text{-------} \\ \text{Solution } C_1 \text{ at } T_2 - \text{Solution } C_2 \text{ at } T_2 \text{-------} \end{array}$$

Here C_1 and C_2 represent the concentrations of the solutions. Since the *osmotic pressure*, the *solution pressure*, and *transference numbers* are functions of the temperature, the electromotive force of a thermoelectric cell cannot be calculated in a simple manner. For further considerations of this point the reader is referred to the original work of Nernst,[1] in which this theory was first developed.

Another kind of thermoelectric cell is that discovered by Seebeck

[1] *Ztschr. phys. Chem.*, **4**, 169 (1889).

in the year 1821, in which only conductors of the first class enter. The following arrangement represents such a cell: —

First metal at T_1 — Second metal at T_1
First metal at T_2 — Second metal at T_2

These cells are of special importance since by means of them the numerical values of the potential-differences between the metals may be determined.

Since a thermoelectric cell generates an electric current only by the change of heat into electrical energy, the equation given on page 225 applies: —

$$\frac{\Pi}{T} = \frac{d\Pi}{dT}; \quad \Pi = T\frac{d\Pi}{dT},$$

and this applies equally well to the combination as a whole as to the individual potential-differences, since a cell can always be conceived in which there exists only the potential-difference considered. It is, therefore, only necessary to know the change of the potential-difference with the temperature $\left(\frac{d\Pi}{dT}\right)$ at the point of contact between two metals, in order to be able to calculate Π, or the potential-difference at the temperature T. The value of $\frac{d\Pi}{dT}$ may be directly obtained from the electromotive force of a thermoelectric cell consisting of the two metals in question, the temperature at one contact point being T, and that at the other $T + dT$. If the temperature T is common throughout, the electromotive force is zero, as the two potential-differences are equal and opposite. It is only because one of the potential-differences may be changed by a temperature change that the electromotive force assumes a certain value, namely, that of the alteration in the potential-difference. From the formula it is evident that if dT is unity, the electromotive force of the cell is $Td\Pi$.

The values of Π, calculated for pairs consisting of the most widely differing metals at the ordinary temperature, are very small, and amount, even in exceptional cases, to but a few hundredths of a volt. In the preparation of thermoelectric piles the latter metals or alloys are especially valuable. A notably high electromotive force, namely, from 0.2 to 0.3 of a volt, results from the combination,

Copper sulfide — Copper,

if the point of contact is heated to about 500° t.

It may be wondered whether or not it would be possible to produce electrical energy commercially by means of thermoelectric piles instead of steam engines. In each case, the process which furnishes the energy is the passage of heat from a higher to a lower temperature. The maximum efficiency may, in each case, be calculated in the same manner with the aid of the second law of energetics. The pile equals the steam engine in simplicity and excels it especially in that it may operate through a greater temperature difference. As a matter of fact, there is a possibility of making such a change from the steam engine to the thermoelectric pile, even if at present it is not feasible because of the expense of construction, of the great loss of heat by conduction, and of the consumption of a part of the electrical energy produced (which means that the quantity of work obtainable from this electrical energy is decreased) in overcoming the great internal resistance of the pile. Furthermore, recent experiments seem to indicate that the problem of transforming heat into electrical energy in this manner is not at all hopeless.[1]

The results of the calculations of the electromotive force which have been carried out are in good agreement with the assumption, made earlier, that the chief source of the electromotive force of a cell is the contact surface between the electrode and electrolyte. It seems, however, upon a closer consideration of actual measurements, that the deduction itself is not satisfactory, at least in some cases; for the measurements show that the electromotive force is not always, but only in the case of certain metal combinations and within narrow temperature limits, proportional to the absolute temperature.

Many thermoelectric couples show so-called reversal points, *i.e.* their electromotive forces decrease with rising temperature, finally becoming zero. The current then changes its direction. Other processes besides those assumed must, therefore, take place at the point of contact of the two metals.

At all events, there is no reason for supposing a considerable potential-difference to exist between metals; while, on the contrary, the existence of slight potential-differences has been shown to be probable.

The law of the electromotive series must evidently apply to the minute potential-differences existing between the metals themselves. A cell composed of only two metals cannot, therefore, generate an electric current when the temperature is the same throughout.

[1] *Ztschr. Elektrochemie*, **9**, 91 (1903).

This conclusion is necessitated by the second law of energetics. Otherwise any desired quantity of heat at constant temperature could be changed into electrical energy without any permanent alteration taking place in the system; which is equivalent to saying that a cyclical process may continually change heat into work. That this electromotive series exists does not explain that discovered by Volta, since in the latter the forces are very much greater. Volta thought that the potential-difference now ascribed to the surface between liquid and metal was really produced at the contact point between the metals. To corroborate his conclusions, the existence of a similar law governing the potential-differences at the surface between metals and liquids must be demonstrated.

In the following pages it will be seen that, theoretically, a certain definite potential-difference exists between a metal and an electrolyte. If, for example, zinc, in contact with an electrolyte whose potential is zero, exhibits a potential of 3, while that of cadmium is 2 and of copper 1, then, according to the electromotive series, the potential-difference between zinc and copper must be equal to the sum of that between zinc and cadmium and that between cadmium and copper. As this is actually the case, the law of electromotive series may be considered correct.

The electromotive series is roughly applicable to galvanic cells. The arrangement,

$$\left.\begin{array}{l} Zn - ZnSO_4 \text{ solution} - CdSO_4 \text{ solution} \\ Cu - CuSO_4 \text{ solution} - CdSO_4 \text{ solution} \end{array}\right\rangle Cd,$$

in accordance with this law, should exhibit the same electromotive force as the arrangement,

$$\left.\begin{array}{l} \text{Zinc} - \text{zinc sulfate solution} \\ \text{Copper} - \text{copper sulfate solution} \end{array}\right\rangle ,$$

if the concentrations of the zinc and copper sulfate solutions are the same in both cases. This is, however, only exceptionally the case. Because of the potential-differences which exist in most cases at the point of contact of two liquids, the law is only approximately true. That the law applies to simple liquid cells only in a certain definite case, has already been mentioned.

CHEMICAL CELLS

The cells thus far described, in which the electrodes are always of the same nature, may in most cases be characterized as *concentration*

cells. To be distinguished from these cells are those in which the electrodes are different and in which chemical energy is transformed into electrical energy. They may be called *chemical cells.* A type of this latter class is the well-known Daniell cell,

Zinc — $ZnSO_4$ solution ----------
Copper — $CuSO_4$ solution --------

When in activity, zinc passes from the metallic into the ionic, and copper from the ionic into the metallic state. In this process (in contradistinction to the ideal concentration cells) a change in the internal energy of the system takes place, and this difference in energy may be considered as the principal source of the electrical energy produced. Instead of the change of positive ions to metal at one pole, and the metal to ions at the other, the negative ions may also perform this process. The cell,

Oxygen (platinized Pt) — KOH solution --------
Chlorine (platinized Pt) — KCl solution ---------

causes hydroxyl ions to be produced in the alkali solution and chlorine ions to change into molecular chlorine in the potassium chloride solution. (The current and process may be reversed under certain circumstances.)

Finally, positive ions may form at one electrode simultaneously with the negative ions at the other. An example is seen in the combination,

Zinc — $ZnSO_4$ solution ----------
Chlorine (platinized Pt) — KCl solution -------

It is also well to remember that in all such cells there is always a small potential-difference produced at the surface of contact of the solutions.

As already noted, the electrical energy may be calculated by the Helmholtz equation, from the heat generated by the chemical processes and the experimentally determined temperature coefficients of the electromotive force. The cell during activity yields as electrical energy the maximum work obtainable through the change which takes place in it. This work bears that relation to the heat of the chemical reactions measured in the calorimeter which is given by the Helmholtz equation. As this equation shows, there may be elements in which the chemical or internal energy change is exactly equal to the electrical energy obtained. These may be considered

as machines which, in their action, will change all the energy put into them into another energy form. There are, secondly, cells in which only a portion of the chemical energy is transformed into electrical energy, and these may be looked upon as machines which transform only a portion of the energy introduced into another form of available energy, while the remainder is lost as heat. A third kind of cell is also known, by which more electrical energy is produced than corresponds to the chemical reactions taking place, and such elements may be considered as machines transforming not only the applied energy into work, but absorbing and changing into work the heat of the surroundings. Imagine in this last class the amount of work which really comes from the heat of the surroundings continually increased; cells are finally reached in which (as in the concentration cells) the internal energy remains unaltered and the electrical energy is derived entirely from the heat of the surroundings. It then becomes a question whether or not these are to be designated chemical cells. From these remarks it may be seen that a sharp line of demarcation between the chemical and other cells does not exist, but one form gradually passes over into the other. The distinction is justifiable in so far as the chemical reaction is the chief characteristic of the cells.

The influence of concentration changes in the electrolytes of any cell upon the electromotive force may be predicted from the principles established for concentration cells. When, for example, the Daniell cell is in operation, zinc ions enter the zinc sulfate solution and copper ions separate out from the copper sulfate solution. If now the concentration of the zinc ions be increased, it is evident that zinc ions can less easily enter the solution. The electromotive force is, therefore, diminished. If, on the other hand, the concentration of the copper ions be increased, the deposition of copper ions is facilitated, and hence the electromotive force is increased. Finally, if the concentrations of the ions in the two solutions are changed equally, the electromotive force remains unchanged, since the effects produced at the two electrodes compensate each other.

In general the rule holds, that the electromotive force of a cell is decreased when, at an electrode, the solution is made more concentrated in respect to the ions which this electrode sends into the solution during the activity of the cell. On the other hand, the electromotive force is increased when the concentration of the ion which *separates* at the electrode is increased. For example, when both solutions of the cell,

Zinc — Zinc sulfate solution
Chlorine — Hydrochloric acid solution

are diluted, the electromotive force is increased.

The magnitude of the change of the potential-difference or of the total electromotive force may be calculated directly from the equation which applies to concentration cells: —

$$E = \frac{RT}{vQ} \ln \frac{P}{P'}.$$

If, for example, only univalent ions are involved and at one electrode the ion concentration 1 normal is replaced by the ion concentration 0.1 normal, the change in the electromotive force is equal to 0.0575 volt at 17° t (see page 200). These conclusions have been finely confirmed by experiment.

The electromotive force of a cell, as already emphasized, is always made up of the sum of at least two separate potential-differences, namely, those which exist at the points of contact of the two electrodes with the liquid of the cell. (In a similar manner, the temperature coefficient of the electromotive force of the cell, $\frac{dE}{dT}$, is the sum of the temperature coefficients of the component potential-differences.) It was endeavored for a long time to find a means of obtaining a knowledge of these component, or single, potential-differences. The results of this endeavor will now be considered.

DETERMINATION OF SINGLE POTENTIAL-DIFFERENCES

By the experimental investigations of Lippmann upon the relation existing between the surface tension of mercury in sulfuric acid and the potential-difference at the point of contact, the measurement of single potential-differences was first made possible. The principal result of Lippmann's research was expressed by him as follows: *The surface tension at the contact surface between mercury and dilute sulfuric acid is a continuous function of the electromotive force of the polarization at that surface.*

Helmholtz later made the researches of Lippmann better understood by an application of the theory of the electrical double-layer. If mercury be brought into contact with a liquid, *e.g.* dilute sulfuric acid, it assumes a positive electrical charge. This may be explained by assuming that the electrolyte contains mercury ions, very possibly from the dissolving of a little oxide, which may be present on the surface of even the purest mercury. The work of Warburg has

also shown that the mercury may be oxidized by the oxygen dissolved in the liquid, and may thus enter the ionic state. Because of its very low solution pressure the mercury itself is positively charged in a solution even when it contains very few of its ions.

At all events, there exists at the surface of contact of the mercury and the solution a certain potential-difference which depends upon the concentration of the mercury ions in the layer of solution directly in contact with the mercury. If now a weak current of low electromotive force be sent from an auxiliary electrode through the solution to the mercury, mercury is deposited and the concentration of the ions is decreased, and the potential-difference is changed by the magnitude of the primary electromotive force, whereupon the current ceases to flow. Since the ion concentration has been decreased, the positive charge of the mercury has decreased and the surface tension increased.

This is the result of the mutual repulsion of the quantities of positive electricity on the surface of the mercury as well as of the negative electricity in the electrolyte, with the consequent expansion of the surface in opposition to the surface tension. If a portion of this electricity be removed, the surface tension naturally increases. By continued increase of the primary electromotive force, a condition may be reached in which the electrical double-layer disappears and the surface is electrically neutral. Evidently at this point the surface tension has reached its maximum value. The potential-difference between the mercury and the liquid is now zero, and the applied electromotive force of the polarizing current is exactly equal and opposed to the single potential of the auxiliary electrode, which may in this way be found. If still more negative electricity be introduced, the mercury becomes negatively charged, and the attracted positive ions of the solution form a new electrical double-layer, differing from the former only in the relative position of the two kinds of electricity. The surface tension of the mercury must now decrease with increased negative charges at the surface because of the mutual repulsion of the quantities of electricity.

The execution of the above experiment is simple in principle; the difficulties which must be overcome in accurate investigations need not be discussed here. The apparatus shown in Figure 46[1] may be used. The capillary *c*, as well as the greater part of the tube *A*, attached to *c* by a rubber tube, are filled with mercury. *c* dips into the cup *B*, which contains a little mercury, and above this is the electrolyte. The position of the mercury in the capillary is observed by

[1] *Ztschr. phys. Chem.*, **15**, 1 (1894).

means of a microscope. The bulb *G*, which contains mercury, permits of the application of desired pressures through its elevation and depression; it is attached to the manometer *M* by a rubber tube. A bent glass tube *D* leads from the latter to *A*, the connections being made with short pieces of rubber tubing. Paraffin oil serves as the liquid of the manometer, increasing the delicacy of the reading. A small vessel, as shown at *F*, containing both paraffin oil and mercury, is connected to the apparatus between the manometer and rubber tube. *P* is an arrangement for impressing any desired potential-difference on the mercury in the capillary tube.

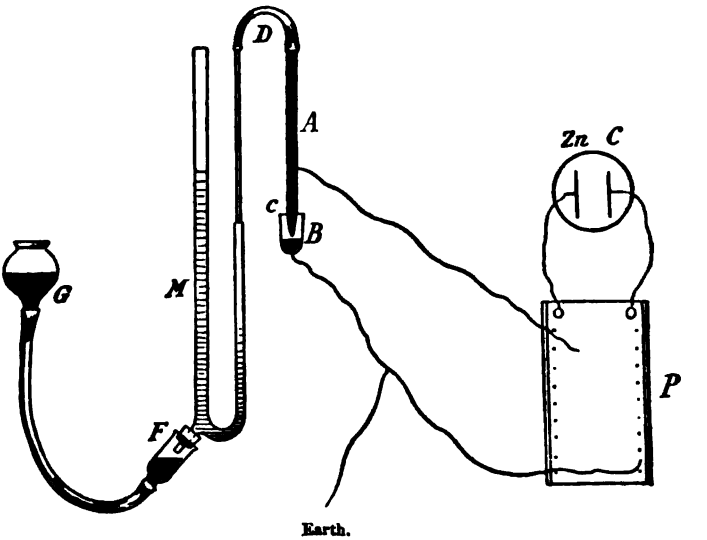


FIG. 46

It is to be recalled that when a capillary is placed in water, the latter rises to a level above that of the surrounding liquid, as it wets the surface of the glass. On the other hand, with mercury the level in the capillary is below that of the surrounding liquid, and, if the surface tension be increased, sinks still lower, that is, it moves against the pressure of the mass of mercury. It is only in this way that a diminution of the surface, the result of increased surface tension, can occur.

If now a certain potential from the source of electricity *P* be applied to the mercury in the capillary *c*, the surface tension of the mercury increases and the meniscus begins to rise. In order to hold this in its original position, a certain pressure must be exerted by

means of the manometer. As the applied potential-difference is increased the necessary pressure also increases, until at a certain potential-difference a maximum in the pressure is observed, which, on further increase of the potential-difference, again diminishes. The potential-difference corresponding to the maximum pressure is that which is naturally assumed by the large mercury surface, the auxiliary electrode, in the electrolyte at *B*.

In order that the results may not be variable, it is necessary to add some mercury salt to the electrolyte, that this may have a certain concentration of mercury ions throughout, since the potential-difference at the surface of the metallic mercury is dependent thereon. The question is naturally raised: Is not the electrode an unpolarizable one when sufficient mercury ions are present, *i.e.* is it not an electrode the potential-difference of which remains nearly constant during electrolysis? In answer, attention is directed to the following: By adding mercury ions to the liquid, the mass of mercury in *B*, the auxiliary electrode, becomes a nearly unpolarizable electrode, which maintains the same potential-difference towards the electrolyte, no matter what other potential-differences are inserted at *P*. Because of its small surface the metallic mass in the capillary only comes into direct contact with a very small part of the electrolyte. Consequently, on the application of a potential-difference, only very few mercury ions pass from the electrolyte into metallic mercury, and new ions can diffuse into the layer at the surface but slowly; therefore this electrode is practically polarizable. Evidently, *the relative extent of the surfaces of mercury, or, better, the relative density of the currents at the two mercury surfaces, plays the important part.* What is actually measured is the potential-difference at the larger mercury surface, since this alone is constant. When the two quantities of mercury are connected by a conductor, that in the capillary changes its surface tension until it possesses the same potential-difference as the lower mass. This is essential to the equilibrium which the current first flowing tends to establish. This is particularly evident when the larger electrode is an amalgam instead of pure mercury. For instance, if it be copper amalgam and the solution above it contains a copper salt, the potential-difference between metal and liquid will be less than before, since the amalgam assumes a less positive charge. The mercury in the capillary again assumes the potential of the lower electrode when the two are connected, and on introducing independent potential-differences a lower value than with pure mercury is sufficient to bring about the maximum surface tension.

By this method it is possible, by avoiding the potential-difference which occurs at the point of contact of the two liquids by a suitable choice of electrolytes, or by applying a calculated correction (see page 219) for this potential-difference, to determine the single potential-difference,

Mercury—Electrolyte,

and, further, neglecting the potential-difference between the two metals, to determine any potential-difference,

Metal—Liquid.

The method of procedure is as follows: The potential-difference, for example, of

$$Hg - HgCl \text{ (solid) in } KCl,\ C_m$$

is first determined. The value found is 0.56 volt, when the electrode is positively charged. This combination, or electrode, is then connected with the combination of which the potential-difference is desired. Supposing the potential-difference

$$Ag - AgNO_3,\ C_n,$$

to be desired, the electromotive force of the combination,

$$\begin{matrix} Hg - HgCl \text{ (solid) in } KCl \text{ solution, } C_n \text{----} \\ Ag - AgNO_3 \text{ solution, } C_n \text{----------} \end{matrix}$$

would be measured. If, from this value, the potential-difference between mercury and potassium chloride solution (0.56 volt) be subtracted, the required value is obtained.

In this connection, the investigations of Rothmund[1] with the Lippmann method are of interest. Instead of mercury, he used amalgams of the base metals, which even at a concentration of about 0.01 per cent exhibit the potential of the pure metal. He measured the potential-differences of the combinations,

$$\begin{matrix} \text{Pb amalgam} - H_2SO_4,\ C_n, \text{ sat. with } PbSO_4 \text{——}, \\ \text{Cu amalgam} - H_2SO_4,\ C_n, + CuSO_4,\ 0.01\ C_m \text{——}, \\ Hg - H_2SO_4,\ C_n, \text{ sat. with } Hg_2SO_4 \text{——}, \end{matrix}$$

and also of the cells formed by connecting the latter combination with the others in succession. He then compared the latter values with the sum of the corresponding single potential-differences. The values obtained are given in the following table: —

[1] *Ztschr. phys. Chem.*, 15, 1 (1894).

Amalgams	Electrolyte	Single Potent.-Diff.
Copper	H_2SO_4 (1 C_n) + $CuSO_4$, 0.01 C_n,	0.445 volt
Mercury	H_2SO_4 (1 C_n) saturated with Hg_2SO_4	0.926 volt
Lead	H_2SO_4 (1 C_n) saturated with $PbSO_4$	0.008 volt

The electrodes were positively, and the electrolyte negatively, charged.

According to the above values, the electromotive force of the

Copper — Mercury cell = 0.481 volt,
and of the Lead — Mercury cell = 0.918 volt.

The values actually measured are 0.458 and 0.923 volt, respectively. In other cases the agreement between the value of the electromotive force taken as the sum of the two single potential-differences and that actually measured was less satisfactory.

To sum up, the following should be noted: The theory which has been outlined is based on the supposition that the surface tension of the mercury is related to the electrical double-layer at its surface only in the way already described, and especially that the nature of the ions forming one side of the double-layer, as well as the nature of the electrolyte in the general, is without influence upon the surface tension of the mercury. Since, however, according to recent investigations of Nernst, the surface tension of the mercury, in contradiction to the theory, is strongly influenced by nonelectrolytes, the theory and therewith the significance of the experimental results is rendered uncertain. Furthermore Billitzer,[1] together with other objections to the theory, has called attention to the fact that the electrolytic solution pressure of mercury must not be considered as a constant, but as a variable increasing with the surface tension.

There is a second method which can be used for the determination of single potential-differences, the principle of which was explained by Helmholtz. Ostwald[2] first showed that it could be used for this purpose, and through his efforts, as well as those of Paschen, the method has been developed.

If an insulated mass of mercury be allowed to flow in a stream through a fine opening and drop into an electrolyte, there can be, according to Helmholtz, no potential-difference between the mercury

[1] *Ztschr. phys. Chem.*, 48, 513 (1904), and 51, 166 (1905).
[2] *Ztschr. phys. Chem.*, 1, 583 (1887).

and the electrolyte. Helmholtz expressed himself on this point in the following manner: —

"Consequently I conclude that when a quantity of mercury is connected with an electrolyte by a rapidly dropping fine stream of the mercury, and is otherwise insulated, the two cannot possess different electrical potentials, for if a potential-difference did exist, for example, if the mercury were positive, each falling drop would form an electrical double-layer on its surface, requiring the removal of positive electricity from the mass, and diminishing its positive charge until that of the mercury and solution reached equality."

An experiment by A. König has already shown that the charge on the mercury can be partly removed by allowing it to drop through a solution. This result was later confirmed in other ways. Figure 47 represents the arrangement employed by König. The mercury cup *a*, beneath dilute sulfuric acid, was connected by a wire with mercury dropping from the capillary into the acid. A galvanometer G was connected into the circuit as shown. This indicated that the positive electricity was removed with the dropping of the mercury in agreement with the previous explanations. If the upper mercury, through the dropping, be brought to practically the same potential as the solution, the polarizable mercury in the cup has the same potential, and therefore the maximum surface tension. This could be determined by means of an ophthalmometer. As still further proof, a weak electromotive force, positive or negative, on being introduced into the circuit on the wire connecting the two electrodes, caused the surface tension to decrease, since a potential-difference was produced between the liquid and the mercury of the cup.

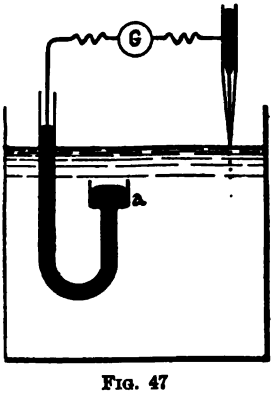


FIG. 47

According to the Nernst osmotic theory, the following statements concerning the drop electrode may be made:[1] If a fine stream of mercury be allowed to flow out of a tube into a solution of an electrolyte containing some mercury salt, as for example mercurous chloride, mercury ions deposit on the fresh surface of the mercury, each drop becomes positively charged and surrounded by the negative chlorine ions corresponding to the ions deposited. Arriving at the bottom, it joins the constant mercury surface there and gives up

[1] *Ztschr. phys. Chem.*, **25**, 265 (1898), and **28**, 257 (1899).

the excess of its positive charge by sending mercurous ions into the solution. These ions, with the chlorine ions, which up to this time constituted the outer part of the double-layer, form mercurous chloride again. As a result of this process, the mercury salt is transferred from the upper to the lower part of the solution, thus forming a concentration cell. Since the solution becomes more concentrated below than above, it would be expected that the current would flow through the solution from the upper to the lower part. This is actually the case. Furthermore, it may be stated that the concentration of the mercury ions in the upper part of the solution must finally become so small, if no diffusion takes place, that the potential-difference there will be zero. This state is not changed nor is there a further transference of salt from the upper to the lower part of the solution when more mercury is allowed to drop through the solution.

The end sought has, then, been attained; for by throwing an electromotive force into the circuit, the potential-difference of the lower mercury electrode can be measured.

As a matter of fact, however, the presence of diffusion prevents a complete freedom of electric charge, and thus causes the measurements to be both difficult and uncertain. However, all errors arising from the fact that an electric charge is still present may be avoided by a method recently proposed by Nernst. It depends on the preparation of a solution of so small a concentration of mercury ions that the potential-difference between it and a mercury surface is equal to zero. A means of preparing such a solution is offered by potassium cyanide. It has been found that in a concentrated solution of potassium cyanide, the direction of the current is reversed, *i.e.* it flows from the stationary mercury through the solution to the mercury drops. If now a solution of potassium cyanide of such a concentration be prepared that no electric current is produced when mercury is allowed to drop through it, the desired zero electrode is obtained. Experimental results obtained by Palmaer[1] have confirmed the correctness of this conclusion. With the use of a zero electrode made as above described, he obtained nearly the same value for the single potential-difference,

$$Hg - KCl,\ 0.1C_n,\ \text{saturated with } Hg_2Cl_2$$

as he did with the aid of the capillary electrical method.

In view of this work, it might with good reason have been thought

[1] *Ztschr. Elektrochem.*, 9, 754 (1903).

that the values so found although questioned are yet near the correct one.[1] The recently published investigations of Billitzer,[2] however, which lead to entirely different values, diminished even more the probable correctness of the values obtained by the above methods.

As has already been explained in Chapter VI, at the surface of contact of a solid and a liquid there is always formed, according to Helmholtz, an electrical double-layer. Hence an electrically charged particle which is suspended in an electrolyte through which an electric current is flowing, will, according to the nature of its charge, migrate toward the positive or toward the negative pole. If all other influences which also may cause the particle to move be excluded, then the sign of the charge upon the particle may be known from the migration direction of the particle, and, further, it may be concluded that at that point at which the direction of migration is reversed, *i.e.* the point at which the double-layer disappears, a system of two bodies with a potential-difference between them equal to zero exists. If the solid particle is a metal, the system is a zero electrode which may be used directly for the determination of the single potential-difference of any other electrode and its solution.

The investigations were carried out with colloidal platinum, silver, and mercury, and also with fine metallic wires with one end fused forming a small sphere, which were suspended perpendicularly from a quartz thread. The movement took place and the reversal could in every case be brought about by changing the ion concentration, in agreement with the Nernst equation relating to the potential-difference between a metal and its solution. The same results were obtained by reversing the experiments. When metallic powder was allowed to fall through a tube containing a solution, an electric current was obtained. The direction of this current could be changed by changing the ion concentration of the solution.. At a definite concentration, by the first method the particles or wires ceased to move, and by the second method the electric current ceased to flow.

It is very remarkable that the value of the potential-difference of the mercury electrode in contact with a normal solution of potassium chloride saturated with mercurous chloride, as measured by the method just described, differs from that obtained by the surface tension method by not less than 0.74 volt. Since, however, the value

[1] See also Krüger, "Theorie d. Elektrokapill. und d. Tropfelektr.," Gotting. Ges. d. Wiss., 1904, Vol. 1.

[2] *Ztschr. Elektrochem.*, **8**, 638 (1902), and *loc. cit.*

obtained by the new method may contain errors,[1] Nernst[2] has repeated his recommendation that until the subject is further investigated, the value at present usually given, *i.e.* for the mercury electrode,

$$E_{Hg\,-\,solution} = + 0.56 \text{ volt},$$

be disregarded, and that the potential-difference of the hydrogen electrode with hydrogen at atmospheric pressure and hydrogen ions at one normal concentration, placed arbitrarily equal to zero, be taken as a standard. It should especially be noted that up to the present no special significance has been attached to the absolute zero point of the electrode potentials. Not to the slightest degree has it a significance such as that which the absolute zero point of the temperature scale possesses; for it has not been found possible to find a numerical relationship between solution pressure and other physical properties. Hence, from this point of view, no objection can be raised to the choice of an arbitrary zero point, *i.e.* an arbitrary zero electrode. The choice of the hydrogen electrode as such a zero electrode possesses advantages in the direction of systematization, since a division of the metals into those which do, and those which do not, evolve hydrogen is thereby effected. On the one side there are the metals which are less, and on the other side those which are more, negative than hydrogen, if the metals be considered to be in contact with their respective normal solutions. Finally, hydrogen is the best reducing agent, and in this respect also divides the electrodes into two classes.

A hydrogen electrode of sufficient constancy for general use is easily prepared. It is only necessary to place a well-platinized platinum electrode into a sulfuric acid solution which is normal in respect to hydrogen ions, and to pass a stream of hydrogen into the solution, and past the electrode for fifteen minutes, in order to obtain the correct potential-difference within 0.001 of a volt. The determination of single potential-differences and their signs is then in the main very simple, if the potential-difference which always exists at the place of contact of the two liquids be left out of consideration. The electrode which is to be investigated is connected with the above standard or normal hydrogen electrode, and the electromotive force of the cell thus formed and the direction of the electric current in the cell are determined according to the usual methods. This electro-

[1] *Ztschr. Elektrochem.*, **12**, 192 and 281 (1906).

[2] *Ztschr. Elektrochem.*, **7**, 253 (1900); *Ztschr. phys. Chem.*, **35**, 291 (1900) and **36**, 91 (1901).

motive force is directly the value of the single potential-difference desired, and its sign is plus or minus according as the electrode in question is the positive or the negative pole of the cell. The direction of the current is represented by an arrow.

What has just been stated is illustrated by the following example. If the electromotive force of the cell

$$Zn - Zn^{\cdot\cdot}, 1\ C_m - H^{\cdot}, 1\ C_m - H_2$$

is equal to 0.770 volt, and the electric current flows from the zinc electrode through the solution to the hydrogen electrode, then the single potential-difference between the zinc and the solution of zinc ions is equal to − 0.770 volt. Representing single potential-difference by $\underline{F}$ as will be done from now on, this may be expressed as follows: —

$$\underline{F}_{Zn \rightarrow solution} = -0.770,$$

or

$$\underline{F}_{solution \leftarrow Zn} = +0.770 \text{ volt.}$$

The sign plus or minus is always that of the electrical charge of the first-mentioned component in the equation, *i.e.* in the former equation, the sign of the electrical charge of the zinc, and in the latter, that of the solution of zinc ions.

In the manner just illustrated, any single potential-difference may be determined. Moreover, the electromotive force of a cell composed of any two electrode combinations may be obtained by taking the sum of the single potential-differences of these combinations. It should be noted that the direction of the arrow in the case of single potential-differences is always that of the current when the electrode combination under consideration is connected with the normal hydrogen electrode. If now the two single potential-differences composing a cell be written one after the other in the order in which they are combined in the cell, and if the two arrows have the same direction, then their signs are the same. If the arrows have opposite directions, the signs are unlike. In the latter case, the direction of the current in the cell is that of the larger single potential-difference. This is illustrated by the following equations: —

$$(1)\quad \underset{-0.770}{\underline{F}_{Zn \rightarrow sol.}} + \underset{-0.329}{\underline{F}_{sol. \rightarrow Cu}} = \underset{-1.099}{F_{Zn \rightarrow Cu}},$$

or

$$\underline{F}_{Cu \leftarrow sol.} + \underline{F}_{sol. \leftarrow Zn} = \underset{+1.099}{F_{Cu \leftarrow Zn}};$$

$$(2)\quad \underset{-0.770}{\underline{F}_{Zn \rightarrow sol.}} + \underset{+0.420}{\underline{F}_{sol. \leftarrow Cd}} = \underset{-0.350}{F_{Zn \rightarrow Cd}},$$

or

$$\underset{-0.420}{\underline{F}_{Cd \rightarrow sol.}} + \underset{+0.770}{\underline{F}_{sol. \leftarrow Zn}} = \underset{+0.350}{F_{Cd \leftarrow Zn}}.$$

Hence it makes no difference whether we write

$$F_{Zn \rightarrow Cd} = -0.350, \text{ or } F_{Cd \leftarrow Zn} = +0.350.$$

In either case the meaning is the same and the arrow shows the direction of the current in the couple, *i.e.* from one electrode through the liquid to the other. In the case represented by the latter equations, the current flows from the zinc, the negative pole, through the liquid to the cadmium, the positive pole.

This method of representation is employed in exactly the same way in the case of electrodes which send negative ions into the solution, such as oxygen, chlorine, bromine, etc., electrodes. When these electrodes are in combination with the hydrogen electrode, the single potential difference,

$$\underline{F}_{\text{electrode} - \text{liquid}},$$

receives the positive sign when negative ions are formed, and the negative when they are discharged. By means of this method of representation, which was in principle suggested by Luther, the survey and comprehension of the subject has been greatly facilitated. *It should, however, be noted that it is not in general use in electro-chemical literature.*

Although the hydrogen electrode possesses certain advantages as a standard electrode, it is not always to be recommended for general use in the measurement of single potential-differences. When used in carrying out measurements with neutral or very concentrated alkaline solutions, diffusion potential-differences of considerable magnitude arise, due to the great difference in the migration velocities of the ions, which can be calculated only with difficulty if at all. In such cases the so-called calomel electrode, which is very constant and easily duplicated, possesses advantages over the hydrogen electrode.[1]

A form of the calomel electrode such as is shown in Figure 48 may be prepared in the following manner:[2] At the bottom of a small upright vessel, about eight centimeters in height and from two to three centimeters in diameter, a small quantity of pure mercury is placed and then covered with a layer of mercurous chloride. The

[1] See also the discussion, "Ueber die Zahlung der Elektrodenpotentiale," *Ztschr. Elektrochem.*, 11, 777 (1905).

[2] For further particulars see Ostwald-Luther, *Physik-chem. Messungen*, page 381.

vessel is then filled with a normal solution of potassium chloride and closed with a rubber stopper carrying two glass tubes. Through one of the latter, a platinum wire is connected with the mercury. The other tube, bent as shown in the figure, is, together with the rubber tube attached to it, filled with the solution of potassium chloride. The bent glass tube *B* of the calomel electrode thus made, is dipped into the liquid of the electrode combination the potential-difference of which is desired, and the electromotive force of the cell thus formed is measured as usual. If the potassium chloride solution produces a precipitate with the solution of the electrode combination under consideration, as would be the case, for example, if the latter contained a solution of silver nitrate, a third and indifferent solution, *e.g.* of potassium or ammonium nitrate, must be introduced between them. It is often advantageous to use a solution of potassium chloride because, since the migration velocities of the respective ions are nearly the same, there is no tendency to form a large potential-difference at the place where the two solutions meet. Since the value of this potential-difference cannot always be calculated with certainty, it is a disagreeable factor in the measurement of single potential-differences. In the case of a contact between a solution of potassium chloride and one of a neutral salt, however, its value is sufficiently small to be neglected. Even when it cannot be neglected, it may easily be made calculable.[1]

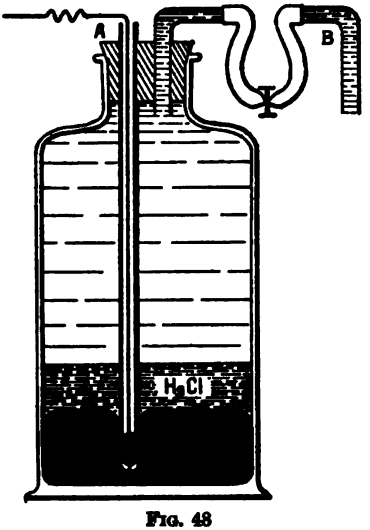


FIG. 48

It was recommended by the International Congress at Berlin[2] that in all cases the directly measured values be given, and that the 1 normal calomel, or the above-defined Nernst hydrogen, electrode be employed as the auxiliary electrode. Following these recommendations, the correct measured values will always be available for possible future recalculation. These values may be considered as single potential-differences referred to the hydrogen or the calomel

[1] Sammet, *Ztschr. phys. Chem.*, **53**, 668 (1905).

[2] *Ztschr. Electrochem.*, **9**, 686 (1903).

electrode as a zero electrode. In this case it must be borne in mind that these values still include the potential-differences which exist at the point of contact of the two solutions.

In the following table are given the most reliable values of the single potential-differences,

$$\pm_{\text{electrode - electrolyte}},$$

when, at room temperature, the electrodes are in contact with their respective solutions containing one ion-mol per liter.[1] The ion concentration is in many cases still uncertain.[2]

In column I are given the calculated or measured single potential-differences against the calomel electrode. These values will be represented by $\pm_c$.

In column II are given the calculated or measured values against the hydrogen electrode. They will be represented by $\pm_h$.

The values inclosed in parentheses have been calculated solely from heat effects.

Since the potential-difference between the calomel and the hydrogen electrode is equal to 0.283 volt, and since in this combination the current flows from the hydrogen electrode through the solution to the mercury, the following relation exists,

$$\pm_{\text{Hg} \leftarrow \text{electrolyte}} = +0.283,$$

when the calomel electrode is referred to the hydrogen electrode as zero electrode; and

$$\pm_{\text{H} \leftarrow \text{electrolyte}} = -0.283,$$

when the hydrogen electrode is referred to the calomel electrode as zero electrode. Hence we have the following relation between the values referred to these two standard zero electrodes,—

$$\pm_h = \pm_c + 0.283 \text{ volt.}$$

This series may at least be considered as the approximately correct *electromotive series*. The values are often called "*electrolytic potentials*" and represented by the letters (EP) when they refer to

[1] Wilsmore, *loc. cit.* The values for Fe, Co, and Ni were obtained from the work of Muthmann and Fraunberger, "Math.-phys. Kl. d. K. Bayr. Ak. d. W. 34," Vol. 2 (1904); those for Ag and O under atmospheric pressure against 1 normal OH' from an investigation of Lewis, *Ztschr. phys. Chem.*, **55**, 473 (1906); and those for Cl, Br, and I from an investigation of Luther and Sammet, *Ztschr. Elektrochem.*, 11, 295 (1905). The latter values were obtained by extrapolation and are referred to a halogen concentration of one mol per liter.

[2] Abegg-Labendzinski, *Ztschr. Elektrochem.*, 10, 77 (1904).

ELECTROLYTIC SINGLE POTENTIAL-DIFFERENCES

Elements		I (E_c)	II (E_A)
Potassium		(−3.48)	(−3.20)
Sodium		(−3.10)	(−2.82)
Barium		(−3.10)	(−2.82)
Strontium		(−3.05)	(−2.77)
Calcium		(−2.84)	(−2.56)
Magnesium		(−2.82)	(−2.54)
Magnesium		−1.774 ?	−1.491 ?
Aluminium		−1.559 ?	−1.276 ?
Manganese		−1.358	−1.075
Zinc		−1.053	−0.770
Cadmium		−0.703	−0.420
Iron		−0.940 [1]	−0.660 [1]
Thallium		−0.605	−0.322
Cobalt		−0.730 [1]	−0.450 [1]
Nickel		−0.880 [1]	−0.600 [1]
Tin		< −0.475	< −0.192
Lead		−0.431	−0.148
Hydrogen		−0.283	± 0.000
Copper		+0.046 [2]	+0.329
Arsenic		< +0.010	< +0.293
Bismuth		< +0.108	< +0.391
Antimony		< +0.183	< +0.466
Mercury		+0.467	+0.750
Silver		+0.515 [1]	+0.798
Palladium		< +0.506	< +0.789
Platinum		< +0.580	< +0.863
Gold		< +0.796	< +1.079
Fluorine		(+1.68)	(+1.96)
Chlorine	25°	+1.120	+1.400
Bromine	25°	+0.812	+1.096
Iodine	25°	+0.345	+0.628
Oxygen		+0.110	+0.393

room temperature. According to the Nernst equation (see page 183), for a metallic electrode,

$$(E_P) = -\frac{RT}{v\underline{e}} \ln P,^{2}$$

since in the above measurements P has been made equal to unity. Hence in general the potential-difference which exists between an electrode and a solution of an ion concentration P, at a temperature T, is as follows:—

[1] Approximately.

[2] The sign becomes + when negative ions are formed.

$$E_{\text{electrode-electrolyte}} = (\text{EP}) + \frac{RT}{v\mathfrak{Q}} \ln P,$$

when the electrode sends positive ions, and

$$= (\text{EP}) - \frac{RT}{v\mathfrak{Q}} \ln P,$$

when it sends negative ions, into the solution.

The electrolytic potentials for solvents other than water cannot yet be given, since the degrees of dissociation involved are not known. The potential-differences of a large number of couples with organic solvents have been measured by Kahlenberg.[1]

Finally, attention is called to the fact that the Helmholtz equation,

$$E\mathfrak{Q} - Q = \mathfrak{Q}T\frac{dE}{dT},$$

is applicable, not only to the electromotive force of the entire cell, but also to the constituent potential-differences of each individual reversible electrode. This has been shown to be true experimentally by Jahn[2] for several metal electrodes. In this equation Q represents the heat effect of the reaction at the electrode in question, and $\frac{dE}{dT}$ the temperature coefficient of the potential-difference in question. Just as the total electromotive force of the cell is made up of two or more independent potential-differences, so the temperature coefficient of the former is made up of the sum of the individual temperature coefficients of the latter.

The expression, $$\mathfrak{Q}T\frac{dE}{dT},$$

represents what is known as the Helmholtz — or Peltier — heat effect. It was first applied to simple metallic contacts. In the case of such contacts, the Peltier effect is understood to mean the quantity of heat which is evolved or absorbed when, at the temperature of the contact, a unit quantity of electricity passes through the contact. The Peltier effect is the reverse of the thermoelectric phenomenon discovered by Seebeck which was mentioned on page 228.

Influence of Negative Ions upon the Potential-difference: Metal — Metal Salt Solution. — The question may still be asked: Is the nature of the negative ion without influence upon the potential-difference? To answer this question, Neumann prepared 0.01 nor-

[1] *J. Phys. Chem.*, **3**, 379 (1899).

[2] *Ztschr. phys. Chem.*, **18**, 399 (1895).

mal solutions of over twenty different thallium salts (mostly of organic acids), and determined the potential-differences between them and pure metallic thallium. In these solutions, these salts may be considered to be equally dissociated, and the same potential-differences might be expected in each case. As the measured values do not differ by more than 0.001 of a volt, it is a justifiable conclusion *that the nature of the negative ion is without influence upon the potential-difference between metal and solution.*

Nevertheless nitrate solutions differ considerably from chloride solutions. These apparent exceptions to the above-stated generalization may be explained by the fact that in the latter case the concentration of the thallo ions, which determine the potential-difference, is less than in the former case, due to the formation of complexes. On the whole, such an indirect influence of the anion is not seldom in the case of metal salt solutions. The degree of complex formation depends on the electro-affinity of the anion.[1]

CELLS IN WHICH THE ELECTROMOTIVELY ACTIVE SUBSTANCES ARE NOT ELEMENTS

A class of chemical cells, apparently very different from that represented by the Daniell element, will now be considered. If a platinized platinum electrode is surrounded by a solution of stannous chloride, and another by one of ferric chloride, and the two are placed in metallic connection, an electric current is obtained, which passes through the cell from the former solution to the latter. The trivalent ferric ions give up an equivalent of electricity, becoming ferrous ions, while each stannous ion takes up two electrical equivalents, becoming a stannic ion, as follows: —

$$Sn'' + 2\,Fe''' = Sn'''' + 2\,Fe''.$$

The process may be imagined in detail as follows: The stannous ions change into stannic, and thereby positive electricity is consumed. This is shown by the equation,

$$Sn'' + 2\,\underline{\ominus}(+) = Sn''''.$$

Since this can never take place alone in a change of chemical into electrical energy, the same quantity of negative electricity must be produced upon the electrode. This electricity passes through the wire to the other electrode, where it unites with the positive

[1] Abegg-Labendzinski, *Ztschr. Elektrochem.*, 10, 77 (1904).

electricity derived from the change of ferric into ferrous ions, according to the equation,

$$2\,Fe''' + 2\,\ominus(-) = 2\,Fe''.$$

The cell

Hydrogen (in platinum) — electrolyte *A*---,
Chlorine (in platinum) — electrolyte *B*----!

is evidently completely analogous to the above combination. It was previously stated (page 194) that platinized platinum in hydrogen may be considered as a hydrogen electrode. In a similar manner the above combination may be characterized as stannous and ferric electrodes, and just as a tendency to go into the ionic (or of the ions to go into the neutral) state was ascribed to the hydrogen and chlorine electrodes, so a tendency of the stannous and ferric to form stannic and ferrous ions may be recognized. The electromotive force of this cell also consists principally of the two independent potential-differences occurring at the electrodes. But these potential-differences depend not only upon the *transformatian pressures* (which are analogous to the solution pressure) of the substances in question, but also upon the osmotic pressures of the ions forming. Therefore the concentrations of the stannic ions formed at the one electrode, and of the ferrous ions at the other, are important factors; a certain constant potential-difference, as in the Daniell cell, could only be expected when the solutions already contained stannic and ferrous ions. Moreover, the concentration of the altering compounds must be considered, for the transformation pressure of a substance at constant temperature is invariable only at a definite concentration.

From what has been said, it is obvious that there is essentially no difference between the Daniell and the so-called reduction and oxidation cells. The laws governing the former may be expected to control the latter.

Already in the first edition of this book (1895) this same explanation was given. At that time, however, a proof of them was not possible because of lack of experimental results. Thus the influence of the concentration of the substances formed at the electrodes has been almost entirely neglected, and it is probable that the varying values of such cells are due to this. The non-reversibility of these cells may be similarly accounted for. If, instead of allowing the stannous chloride — ferric chloride cell to act, it be opposed by a cell of greater electromotive force, oxygen must separate at one electrode (at least in dilute solution) and metallic tin at

the other. Stannic and ferrous chlorides being present, a change of the stannic into the stannous, and of ferrous into ferric salt, when the current is not too strong, would certainly take place instead of the above, and the cell be reversible.

A cell which consists of zinc and chlorine electrodes, and of electrolytes which do not contain zinc and chlorine ions, is also not a reversible cell. If a stronger opposing current be sent through such a cell, the positive ions of one electrolyte separate at the zinc, and the negative of the other at the chlorine electrode, while zinc and chlorine ions are liberated through its own activity as a cell.

Equations may be deduced for the calculation of the electromotive force of such cells. They are analogous to those formulated for the Daniell cell.[1]

Every process which takes place at an electrode of a cell during its activity may be represented by the following scheme:—

$$aA + bB \cdots + v\underline{\varepsilon}\ (+) \rightleftarrows dD + eE \cdots.$$

Here a b, $\cdots$ represent the number of mols of the substances A, B, $\cdots$ which by taking on the quantity of positive or giving off the quantity of negative electricity, $v\underline{\varepsilon}$,[2] form d, e, $\cdots$ mols of the substances D, E, $\cdots$. By an application of this scheme to the ferri-ferro electrode, the following equation is obtained:—

$$Fe'' + \underline{\varepsilon}(+) \rightleftarrows Fe'''.$$

The left-hand side of this equation represents the higher state of reduction or the lower state of oxidation. The upper arrow of the transformation sign, then, represents an oxidation, while the lower one represents a reduction.

As already indicated, the assumption that the potential-difference at the electrode, not only in the case of the Daniell cell but in general, is dependent on the concentration of the substance being formed as well as on that of the substance being consumed, in the manner required by the Nernst logarithmic equation, seems plausible. If all the substances under consideration be taken at unit concentration, *i.e.* usually one mol (or one ion-mol) per liter, and if the value in this case of the potential-difference,

$$E_{\text{electrode - electrolyte}}$$

[1] See also Ostwald-Luther, *Physiko-chemische Messungen*, p. 373; *Ztschr. Elektrochem.*, 7, 1043 (1901).

[2] In passing from metallic to ionic state, v = valence of the ion formed. See also page 182.

be represented by E_0, then, accepting the correctness of the above assumption, the following equation is obtained for the potential-difference at an electrode when the electrolyte is of any concentration C:—

$$E_{\text{electrode}-\text{electrolyte}} = E_0 + \frac{RT}{\nu Q} \ln \frac{C_D^d \times C_E^e \cdots}{C_A^a \times C_B^b \cdots}.$$

The higher state of oxidation is represented in the numerator and the lower state in the denominator. The former, then, becomes transformed into the latter by giving up positive or taking on negative electricity. In regard to the sign of E or E_0, the rule given on page 244 is to be followed. The value of E_0 may also appropriately be considered as the electrolytic potential (EP). For the ferri-ferro electrode, the following equation should hold:—

$$E_{\text{electrode}-\text{electrolyte}} = E_0 + RT \ln \frac{Fe'''}{Fe''},$$

where Fe''' and Fe'' represent the concentrations or the osmotic pressures of the ferro and ferri ions respectively. This expression is entirely analogous to that which holds for metal electrodes. Applied to the hydrogen and chlorine electrodes, the equation assumes the following forms:—

$$E_{\text{electrode}-\text{electrolyte}} = E_0 + \frac{RT}{2Q} \ln \frac{H^{\cdot 2}}{H_2};$$

$$E'_{\text{electrode}-\text{electrolyte}} = E_0' + \frac{RT}{2Q} \frac{Cl_2}{Cl'^2}.$$

For an oxygen electrode, two different expressions hold according as the equation,

$$O_2 + 4Q\ (-) = 2\,O'',$$

or the equation,

$$O_2 + 2\,H_2O + 4Q\ (-) \rightleftarrows 4\,OH',$$

be considered to take place.[1] The equation which holds in the former case is as follows:—

$$E''_{\text{electrode}-\text{electrolyte}} = E_0'' + \frac{RT}{4Q} \ln \frac{O_2}{(O'')^2}.$$

[1] The following relation exists:—

$$2\,OH' \rightleftarrows H_2O + O''.$$

The concentration of the OH ions, but not that of the O ions, can be obtained experimentally. The latter is certainly very small. In a consideration of equilibrium states it makes no difference whether OH′ or O″ ions are involved.

Here E_0'' represents the (EP), or, in words, the potential-difference which exists when the oxygen is under a pressure of one atmosphere and is in contact with a solution which contains one gram-ion of oxygen ions per liter. The equation which holds in the second case is

$$E''_{\text{electrode}-\text{electrolyte}} = E_0''' + \frac{RT}{4\varrho} \ln \frac{O_2}{(OH')^4}.$$

The value of E_0''' is determined by the fact that the oxygen is under a pressure of one atmosphere and is in contact with a normal solution of hydroxyl ions. Strictly speaking, the value H_2O should appear in the numerator of the fraction the logarithm of which is to be taken. Since, however, the concentration of the water is not appreciably changed during the reaction, its mass-action effect can be left out of consideration. In fixing the value of E_0''', the concentration of the water in the solution may be placed equal to unity. It very often happens that water takes part in a reaction in this manner. Assuming that the following reaction takes place at a permanganate electrode,

$$MnO'_4 + 8\,H^{\cdot} + 5\varrho\ (-) \rightleftarrows Mn^{\cdot\cdot} + 4\,H_2O,$$

then the strict equation would be

$$E'_{\text{electrode}-\text{electrolyte}} = E_0 + \frac{RT}{5\varrho} \ln \frac{MnO'_4 \times H^{\cdot}}{Mn^{\cdot\cdot} \times (H_2O)^4}.$$

As in the case of the metals, so in the case of other oxidizing or reducing substances, the determination of (EP) is of importance. Very little in this direction has, however, been done. Below a few accurate values are given: —

ELECTRODE	$E_{\text{ELECTRODE} \leftarrow \text{ELECTROLYTE}}$
Ferri-ferro	+ 0.46 volt
Cupri-cupro	+ 0.13 volt
Ferri-ferrocyanide	+ 0.153 volt
Thalli-thallo	+ 0.908 volt

Measurements have been made to confirm the statement that the electromotive force varies with the concentration of the substances involved as required by the above equation by Peters,[1] Schaum,[2] Fre-

[1] *Ztschr. phys. Chem.*, **26**, 193 (1898).

[2] Sitzber. d. G. zur Beförderung d. Naturw., Marburg, No. 7, 1898.

denhagen,[1] Spencer-Abegg,[2] Maitland-Abegg,[3] and Sammet-Luther.[4] Their results are in good agreement with the theory.

The results given in the last-named investigation will be considered again in the discussion of equilibrium constants. Other (EF) values will then be given. At this point attention will be called only to the possibility of determining the *electromotive valence, i.e.* the number of chemical equivalents of electricity ϱ required for the electrolytic oxidation or reduction of the reacting substances, from the dependence of the electromotive force on the concentration. If the process takes place in stages, as in the case of the reduction of molybdic acid solutions through intermediate pentavalent to trivalent molybdinum, it may be perceived by means of continued potential measurements, the influence of the concentrations of the individual reacting substances being taken into consideration. An insight into the mechanism of electrolytic processes may thus be obtained.[5]

It scarcely needs to be mentioned that, when two single potential-differences are combined to form a cell, the electromotive force of the cell is essentially equal to their sum. This was proven by Bancroft.[6] Although his results suffered from the lack, at that time, of known ion concentrations, the values of the single potential-differences measured are given here because they are of considerable interest and because they are a measure of the strength of the oxidizing or reducing power of the substances. They were obtained with the use of platinized electrodes surrounded by the liquids mentioned. Most of the solutions contain about $\frac{1}{8}$ mol per liter.

It is evident from the preceding discussion that in electrical processes it is possible to distinguish sharply between oxidations and reductions. *In the case of such processes, a substance is said to be oxidized when its positive charge of electricity is increased or its negative charge decreased. It is said to be reduced when, conversely, its negative charge is increased or its positive charge is decreased.*

An actual *oxidation, i.e.* interaction with oxygen, although formerly always believed to take place, is in many cases not involved. The action consists, instead, of a change of the charges on the ions. The term oxidation is, however, still retained.

[1] *Ztschr. anorg. Chem.*, **29**, 396 (1902).
[2] *Ztschr. anorg. Chem.*, **44**, 379 (1905).
[3] *Ztschr. Elektrochem.*, **12**, 263 (1906).
[4] *Ztschr. Elektrochem.*, **11**, 293 (1905); *Ztschr. phys. Chem.*, **53**, 641 (1905).
[5] Chilesotti, *Ztschr. Elektrochem.*, **12**, 173 (1906).
[6] *Ztschr. phys. Chem.*, **10**, 387 (1892), and **14**, 228 (1894).

Solutions of	E^c electrode – electrolyte	Solutions of	E^c electrode – electrolyte
$SnCl_2 + KOH$ . .	– 0.861	$FeSO_4$, neutral .	+ 0.073
Na_2S	– 0.651	Hydroxylamine .	+ 0.076
Hydroxylamine, KOH	– 0.616	$NaHSO_3$	+ 0.103
		H_2SO_3	+ 0.158
Chromous acetate, KOH	– 0.589	$FeSO_4 + H_2SO_4$ . .	+ 0.234
		Potassium ferric oxalate . . .	+ 0.286
Pyrogallol, KOH .	– 0.482		
Hydrochinone . .	– 0.329	I_2, KI	+ 0.328
Hydrogen, HCl .	– 0.311	$K_3Fe(CN)_6$ . . .	+ 0.422
Potassium ferrous oxalate . . .	– 0.275	$K_2Cr_2O_7$	+ 0.502
		KNO_3	+ 0.577
Chromous acetate	– 0.196	Cl_2, KOH . . .	+ 0.626
$K_4Fe(CN)_6$, KOH	– 0.086	$FeCl_3$	+ 0.678
I_2, KOH	– 0.070	HNO_3	+ 0.697
$SnCl_2$, HCl . . .	– 0.064	$HClO_4$	+ 0.707
Potassium arsenate	– 0.054	Br_2, KOH . . .	+ 0.755
		$H_2Cr_2O_7$	+ 0.837
NaH_2PO_2 . . .	– 0.044	$HClO_3$	+ 0.856
$CuCl_2$	+ 0.000	Br_2, KBr . . .	+ 0.865
$Na_2S_2O_3$	+ 0.016	KIO_3	+ 0.929
Na_2SO_3	+ 0.023	MnO_2, KCl . . .	+ 1.068
Na_2HPO_3 . . .	+ 0.033	Cl_2, KCl	+ 1.106
$K_4Fe(CN)_6$ . . .	+ 0.035	$KMnO_4$	+ 1.203

According to these definitions there must be, in every galvanic cell, an oxidation at one electrode and a reduction at the other. In the Daniell cell the reduction takes place at the zinc electrode and the oxidation at the copper. The precipitation of one metal by another, the process of substitution, is thus to be considered as one of oxidation and reduction. It is evident, then, that the metals can only serve as reducing agents, since they are only capable of producing positive ions, followed by the formation of negative or the disappearance of positive ions. The metals themselves are thereby oxidized.

On the other hand, all of those elements which produce negative ions act exclusively as oxidizing agents. Solutions of electrolytes in general may be reducing as well as oxidizing agents, for they contain both positive and negative ions, and are therefore capable of yielding positive or negative electricity. If zinc be placed in a solution of cadmium bromide, cadmium is precipitated, the solution acting as an oxidizing agent; but if chlorine be conducted into the solution, bromine separates, the solution acting as reducing agent.

Similarly, the substances in the above table may be examined to discover whether they are reducing or oxidizing agents. From the above it is, moreover, not surprising that a dissolved substance may have a reducing or oxidizing action according to circumstances. This may even be the case when only the single ion enters the reaction; the bivalent ferrous ion may change into the trivalent ion, on the one hand, or into metallic iron, on the other; that is, it may act reducing or oxidizing.

Attention has been called by Luther[1] to the fact that since the change in free energy in an isothermal, reversible process is independent of the path and dependent only on the original and final states, the work required to transform the lower directly into the highest state of oxidation is equal to the work required to effect the transformation from the lower to the next higher state plus the work required to transform the latter to the highest state of oxidation, etc. Since, now, the work for the reversible oxidation is measured by the quantity of electricity consumed, the following holds: —

$$(a + b)\,\underline{Q}\,\mathrm{E} = a\underline{Q}\,\mathrm{E}' + b\underline{Q}\,\mathrm{E}''.$$

Here a and b represent the numbers of electrical units $\underline{Q}$ of electricity consumed in changing the state of oxidation from the lower to the intermediate, and from the intermediate to the higher state, respectively. The electromotive force required during the first stage of the oxidation is E', and during the second stage E'', while that required when the entire oxidation takes place in one stage is E. From the above equation the following is obtained: —

$$\mathrm{E} = \frac{a\mathrm{E}' + b\mathrm{E}''}{a + b}.$$

In the case of iron, which may furnish either di- or trivalent ions, this equation becomes

$$\mathrm{E} = \frac{2\,\mathrm{E}' + \mathrm{E}''}{3},$$

and in the case of copper, which may furnish uni- and bivalent ions, it becomes

$$\mathrm{E} = \frac{\mathrm{E}' + \mathrm{E}''}{2}.$$

These equations state that the electromotive force which is re-

[1] *Ztschr. phys. Chem.*, **34**, 488 (1900), and **36**, 385 (1901). The numerical values have been changed to agree with more recent measurements. See previous pages.

quired to carry out the oxidation in one stage from the lowest to the highest state, is always between the two electromotive forces which are required to carry out the oxidation from the lowest to the intermediate, and from the intermediate to the highest state, respectively. Hence, such a relation as,

$$E = E' + E'',$$

which at first sight one might hit upon, does not hold.

Nothing can be predicted in regard to the order of the three electromotive forces, since they depend both upon the nature of the substances and upon the concentrations involved. If the latter condition be eliminated by taking all substances involved at a concentration unity, then two typical cases may occur.

Case I. Iron is an example of this case. When two of the values are known, evidently the third one may be calculated. Thus for iron

$$E' = E_{c\ Fe \rightarrow Fe^{\cdot\cdot}} = -0.94 \text{ volt, and}$$

$$E'' = E_{c\ Electrode \leftarrow Electrolyte\ \frac{Fe^{\cdot\cdot\cdot}}{Fe^{\cdot\cdot}}} = +0.46 \text{ volt,}$$

has been found. It follows, then,

$$E = E_{c\ Fe \rightarrow Fe^{\cdot\cdot\cdot}} = -0.47 \text{ volt.}$$

The order is, therefore, E', E, and E'',

or, in other words, the strongest reducing process is that corresponding to E' and the strongest oxidizing process is that corresponding to E''.

Leaving out of consideration the negative ions, in the cell,

$$\begin{array}{l} \text{Iron} - \text{ferrous ions} \text{----------} \\ \text{Platinum} - \text{ferrous and ferric ions} \text{-----} \end{array} \quad (1)$$

the iron electrode is negative, and the platinum electrode positive. When the cell is active, the quantity of iron and ferric ions decreases, while that of the ferrous ions increases. In the cell, therefore, the same action takes place as would take place if the substances at the same concentration were directly mixed, *i.e.* formation of the intermediate state of oxidation at the expense of the other two, according to the equation,

$$2\,Fe^{\cdot\cdot\cdot} + Fe = 3\,Fe^{\cdot\cdot}.$$

Besides the above cell (1), two more may be formed by combining the three potential-differences. They are as follows: —

$$\left.\begin{array}{l}\text{Iron — ferrous ions}\\ \text{Iron — ferric ions}\end{array}\right| \quad (2)$$

and

$$\left.\begin{array}{l}\text{Iron — ferric ions}\\ \text{Platinum — ferrous and ferric ions}\end{array}\right| \quad (3)$$

In these cells also, when a current flows, the intermediate stage of oxidation is formed at the expense of the other two.

There are interesting relations which exist between these three cells. If the electromotive forces of the cells be calculated from the single potential-differences, the following values are obtained: —

Cell	Electromotive Force
(1)	1.40 volts
(2)	0.47 volt
(3)	0.93 volt

If, further, the number of units of electricity $\underline{q}$ which must be passed through each cell in order to dissolve 56 grains of metallic iron be calculated, the values obtained are as follows: —

Cell	Coulombs
(1)	$2\,\underline{q}$
(2)	$6\,\underline{q}$
(3)	$3\,\underline{q}$

Hence the quantity of energy obtainable from the process,

$$2\,Fe''' + Fe = 3\,Fe'',$$

may be obtained in any one of the following three forms according to the cell used: —

Cell	Form
(1)	1.40 volts $\times\, 2\,\underline{q}$
(2)	0.47 volt $\times\, 6\,\underline{q}$
(3)	0.93 volt $\times\, 3\,\underline{q}$

Naturally, the product is in all cases equal to $2.80 \times 96{,}540$ joules. It is evident that here a true galvanic transformation of energy is being dealt with, which is thereby characterized that only such

transformation relations can appear as can be expressed in whole numbers. Whether or not all these cells can be realized is another question.

Case II. Copper is an example of this case. The action is here the opposite of that in the case of iron, *i.e.* the lower and higher states of oxidation increase spontaneously at the expense of the intermediate state, as follows: —

$$2\,Cu^{\cdot} = Cu + Cu^{\cdot\cdot}.$$

When the cell,

Copper — cuprous ions----------
Platinum — cuprous and cupric ions-----

(which, however, cannot be directly realized because of the unstable character of the cuprous ions), is in action cuprous ions must disappear and cupric ions appear. In other words, the platinum pole must be negative and the copper pole positive. Corresponding to this, the order of the electromotive forces is the reverse of that in the case of the iron, being

$$E'',\ E,\ \text{and}\ E'.$$

In this case, the process corresponding to E'' is most strongly reducing, while that corresponding to E' is most strongly oxidizing.

It is characteristic of all such cases as that of copper that on the one hand the intermediate stage $Cu^{\cdot}$ is more strongly oxidizing than the highest stage $Cu^{\cdot\cdot}$, and on the other, it produces a stronger reducing influence than does the lowest stage Cu. Furthermore, other conditions remaining the same, the activity of the intermediate stage both as an oxidizing and as a reducing agent increases with increasing concentration.

Although it sounds paradoxical, by the oxidation of metallic copper a stronger reducing agent $Cu^{\cdot}$, and by the reduction of cupric ions a stronger oxidizing agent $Cu^{\cdot}$, is obtained. In other words, it may be stated that, by the addition of a positive charge, the oxidizing power, and by the removal of a positive charge, the reducing power, of a substance may be increased.

Considering, finally, an iron electrode (the same holds for a copper electrode) in contact with a solution with ferrous and ferric ions in such concentrations that

$$E = E'$$

and equilibrium exists at the electrode. The relation

$$E'' = E = E'$$

is then obtained directly from Luther's equation. Hence when equilibrium is established, the three potential-differences are always equal to each other.

It may be well to say a word here concerning the conditions which determine the actual production of the electric current.[1] It has been seen that in all galvanic cells a reduction and oxidation take place; that is, at one electrode ions come into existence, and at the other ions disappear. *That the reaction may be the source of an electric current, the two processes must take place at points separated from each other.* If they both occur at the same point, no electric current can be obtained. Zinc being placed in a copper sulfate solution, both the oxidation and reduction proceed simultaneously at the surface of the metal. The electric charges of the dissolving zinc and precipitating copper have the opportunity of neutralizing each other there, and the possibility of a removal of this neutralization to some other point (and thereby the production of an electric current) is lost. *Hence the general statement, that a chemical reaction between two substances can only be used as a source of electrical energy when electricity is produced or disappears during the reaction* (i.e. *by changes in the charges of the ions*), *and also when the two substances separated from each other are still capable of undergoing this reaction.*

If zinc be in contact with a solution of zinc sulfate, and a platinum wire be placed therein, only a feeble current is obtained on connecting the wire with the zinc. If it be desired to dissolve the zinc rapidly, that is, to cause it to pass into the ionic state and produce a large current, this may be accomplished by surrounding the *platinum* with a solution such as that of a copper salt, or of an acid whose positive component has a smaller tendency to produce ions than zinc. The addition of the copper or acid solution directly to the zinc solution would evidently not produce an electric current.

In the production of galvanic currents many different oxidizing agents have been used to achieve the highest possible efficiency, without the theory of the phenomena being clearly understood. One of the most common cells is the bichromate cell, consisting of

$$Zn - H_2Cr_2O_7(Na_2Cr_2O_7 + H_2SO_4) - C.$$

The process consists essentially in the formation of zinc ions at the negative (zinc) electrode, and the reduction of chromium ions at the positive (carbon) electrode from higher to lower valency, whereby electricity is given up to the electrode.

[1] Ostwald, "Chemische Fernewirkung," *Ztschr. phys. Chem.*, 9, 540 (1892).

The electromotive force of this cell is great, because the zinc has a strong tendency to go into the ionic state, and the chromium ions of high valency also tend strongly to change into ions of lower valency, the two tendencies additively producing the high electromotive force. Furthermore, it is clear that the electromotive force of this cell, when active, must gradually diminish, because zinc ions are continually forming, while the concentration of the chromium ions of higher valency is decreasing, and that of those of lower valency increasing. Each of the three changes reduces the electromotive force.

The energetic oxidation of the zinc and the high electromotive force of the cell is therefore obtained by the addition of the oxidizing agent, not to the zinc, but to the carbon.

It is also possible to dissolve the noble metals or to change them into the ionic state in a similar manner. A cell consisting of

$$\text{Pt} - \text{NaCl solution} - \text{Au}$$

produces no electric current, though one is produced when chlorine water is introduced at the platinum electrode, the gold dissolving. The great tendency of the chlorine to yield ions may be looked upon as forcing the resisting gold to act similarly. Addition of the chlorine water to the gold electrode alone would not result in the production of a current (the platinum being unaffected), and the gold would oxidize very slowly.

The free energy of other processes, such as that of solution, can be made to produce an electromotive force by being coupled or combined with oxidation or reduction processes.[1] Thus the double cell,

$$\begin{array}{l} H_2(\text{in Pt}) - \text{saturated solution over solid salt} - O_2(\text{in Pt}) \\ H_2(\text{in Pt}) - \text{pure water} - O_2(\text{in Pt}) \end{array}$$

produces an electric current which flows from the saturated solution through the oxygen electrode to the pure water. The process which takes place when the cell is in action is merely the combining of water with solid salt to form a saturated solution. Since this process can in this manner be carried out reversibly, the electrical energy derivable from it gives directly the maximum available work of the process. As a matter of fact, the same relations have been considered, only from a different standpoint, earlier in the book, especially in the section on double concentration cells (see page 211).

Finally, the above cell shows clearly that the active mass of the water in the solution is not, as has been tacitly assumed up to this

[1] Ostwald-Luther, *Hand- und Hilfsbuch*, p. 888.

point, equal to that of pure water. It is proportional to the vapor pressure. In the case of dilute solutions, however, the difference between the active masses of pure water and solution, and therefore also the electromotive force of the cell, is very small. Since the active mass varies, the product $H^{\cdot} \times OH'$ must also change; for if it remained constant, then, considering the above cell as a combination of

Hydrogen----------$H^{\cdot}$-------
and Oxygen----------OH'------

electrodes, no electromotive force could arise.

FORMATION OF POTENTIAL-DIFFERENCE AT THE ELECTRODES. SPONTANEOUS EVOLUTION OF OXYGEN OR HYDROGEN. THE PROCESS OF CURRENT PRODUCTION[1]

In considering any electrode and an aqueous solution of the corresponding ions, between which there exists an electromotive force E, it must not be forgotten that there are also hydrogen and hydroxyl (or oxygen) ions present in the water. Hence in order that equilibrium may be established, each electrode must become charged with hydrogen and oxygen to such an extent that the potential-difference of the combination, —

Hydrogen — hydrogen ions —,

and of the combination, —

Oxygen — oxygen ions —,

is equal to E. In this connection, the reader is referred to the discussion on page 187 and to the note on page 254. This process is of special importance in the case of platinized platinum electrodes, because they dissolve large quantities of gases, and, further, because a state of equilibrium is established in a short time. At a platinized ferri-ferro electrode, for example, the following equilibrium equations must be satisfied: —

$$2\,Fe^{\cdot\cdot} + 2\,H^{\cdot} \rightleftarrows 2\,Fe^{\cdot\cdot\cdot} + H_2,$$

$$2\,Fe^{\cdot\cdot} + \frac{O_2}{2} \rightleftarrows 2\,Fe^{\cdot\cdot\cdot} + O''.$$

If the tri- and bivalent iron ions are of normal concentration in the solution, then the potential-difference, —

$$E_{\text{electrode — electrolyte}} = +0.46 \text{ volt.}$$

[1] See also Fredenhagen, *Ztschr. anorg. Chem.*, 29, 396 (1902.)

It follows from this that, at a given concentration of hydrogen and oxygen ions, the concentrations of the hydrogen and the oxygen in the electrode may be calculated. The latter must, naturally, be changed by a change in the concentration of the hydrogen and oxygen ions if that of the iron ions remains unchanged. A short consideration shows that to a higher charge of oxygen there always corresponds a lower one of hydrogen, and conversely. Now it is evident that when the concentration of the gas in the electrode becomes too great, it escapes from the electrode. Assuming that this takes place if the hydrogen or oxygen exerts a pressure of one atmosphere, then it may be stated that every oxidizing agent for which

$$E_{\text{c electrode - electrolyte}} > 0.94 \text{ volt},$$

or, what is the same thing,

$$E_{\text{a electrode - electrolyte}} > 1.22 \text{ volts},$$

must cause the evolution of oxygen from a solution which is normal in respect to hydrogen ions. This action must, moreover, continue until the concentrations involved have been so diminished as to lower the potential-difference to the value 0.94 or 1.22 volts, according to the standard of reference adopted. On the other hand, a reducing agent for which the potential-difference E_c or E_a is less than -0.283 or 0.00 volt respectively, will cause hydrogen to be evolved from a solution of hydrogen ions of normal concentration. Thus it is seen that oxidizing and reducing agents in aqueous solutions are relatively stable, and capable of measurement only within narrow limits. Outside these limits only states in transition exist, and therefore the deduced equations are no longer applicable. This is true, for instance, of solutions of persulfates which break down into sulfates with the evolution of oxygen. Only when the persulfate concentration becomes very slight is the potential-difference corresponding to its relative stability reached. Relative stability only can be spoken of because all oxidizing and reducing agents undergo such a change with hydrogen and oxygen ions (and consequently with the corresponding charges of gases on the electrode) that their electrode potential-differences always approach that value corresponding to the atmospheric oxygen. Since this oxygen is present in an inexhaustible quantity, its concentration remains constant. The iron electrode mentioned above is in stable equilibrium in the air only when in a solution of such a concentration in respect to the oxygen (or hydroxyl) ions that the electrode of atmospheric oxygen in it also produces a potential-difference of 0.46 volt.

The assumption is here made that the existing hydrogen concentration in the electrode remains unchanged. Since, strictly speaking, this would only be the case when the corresponding pressure of hydrogen exists in the atmosphere, which certainly is not the case, the conclusion is now reached that a state of complete equilibrium is never attained. However, since as long as the pressures of the gases do not exceed one atmosphere they diffuse from the electrode into the surroundings very slowly, it may be assumed in practice that, below this limit, the relations may be calculated.

Another important result may be obtained from these considerations. If for a reducing agent,

$$E_{\text{h electrode - electrolyte}} < 0.00 \text{ volt},$$

it will no longer be stable in a 1 normal solution of hydrogen ions, but will be stable in a solution containing less hydrogen ions, as, for example, in a solution containing hydroxyl ions. The lower the hydrogen ion concentration, the greater (counting negatively) will be the potential-difference between the hydrogen under atmospheric pressure and the solution, and the greater can also be that between the reducing agent and the solution without causing hydrogen to be evolved. The less noble metals, such as iron, furnish the simplest illustration of this behavior. In a 1 normal solution of ferrous ions, which is neutral and therefore contains but few hydrogen ions, iron does not evolve hydrogen. On the other hand, if the solution is acid and therefore contains many hydrogen ions, the iron evolves hydrogen immediately.

An analogous discussion may be applied to the case of oxidizing agents, or substances producing high positive potential-differences. They are more stable and evolve oxygen less energetically and after a longer time in acid than in alkali solutions.

In the previous discussion it was assumed that the potential-difference in the case of such oxidizing or reducing agents as a ferri-ferro solution, the changes of which do not involve hydrogen or hydroxyl ions, is independent of the concentration of these ions, *i.e.* is the same in acid or alkali if the concentration of the ions of the oxidizing or reducing substance is not changed. Within certain limits, experimental measurements have confirmed this assumption. The magnitude of the concentration of the gases hydrogen and oxygen on the electrodes naturally changes, as already explained, corresponding to the changes in the concentrations of the hydrogen and oxygen ions.

If there is a possibility of further reactions taking place at the

electrodes, as would be the case, for example, if iodine be added, then in this case, when equilibrium is again established, the potential-difference between the iodine and iodine ions must be equal to that just considered above. If the electrolytic potential-difference for the individual reactions be known, then very interesting calculations may be carried out. For example, we may calculate the ratio of ferrous to ferric ions which may exist in a normal solution of iodine ions which is saturated with iodine.[1]

If it is so desired, all galvanic cells, especially those with platinized electrodes, may, therefore, be considered as hydrogen and oxygen concentration cells. It is not possible to say with certainty just how in the individual cases the electric current comes into existence. It is, in all probability, different in different cases. In the case of the ferri-ferro electrode it may be assumed, as has been done in the preceding pages, that the current results from the direct transformation of ferric into ferrous ions, but it also seems permissible to assume that the current, or a part of it, results from such a reaction between the ferric and hydroxyl (or oxygen) ions as is represented by the equations given on page 263. As a result of this reaction, the electrode may become laden with hydrogen, and thereupon become electromotively active. In the case of the oxidation of thiosulfate to tetrathionate according to the equation,

$$2\,S_2O_3'' + 2\,\textcircled{+} = S_4O_6'',$$

it has been shown by Thatcher[2] to be very probable that the process only takes place through the agency of oxygen. Likewise in the case of organic oxidizing agents, for example chinone, which are not measurably ionized, the above assumption seems plausible. In an analogous manner, through a reaction taking place at the electrode by which a reducing is transformed into an oxidizing substance, *e.g.* ferrous into ferric ions, the electrode may become laden with hydrogen, and then exhibit an electromotive force. In the case of the metal electrodes we will assume that the current is not produced by such an indirect process, but by the direct passage of the metal into the ionized state, although opposition to this view has already become strong.

There are many metals which, upon being dissolved electrolytically, are capable of forming more than one kind of ions. This fact raises a question as to the nature of the process of solution in such

[1] For further particulars, see Abegg, *Ztschr. Electrochem.*, 9, 569 (1903).
[2] *Ztschr. phys. Chem.*, 47, 641 (1904).

cases.[1] Now the metals must dissolve in such a manner that the potential-differences between the electrode and the various ions shall be the same. The relation between the concentrations of the ions being formed is thereby determined. If another substance, which forms a complex compound with one kind of ions, be added to the solution, it is at once evident that the valence with which the metal goes into solution will be more or less changed in favor of the ion thus constantly removed to form the complex compound. Undoubtedly complications often appear during the solution of metals. They will be considered further in the section on the passive state.

ELECTROMOTIVE FORCE AND CHEMICAL EQUILIBRIUM

When an electromotively active reaction takes place at an electrode, and all effective concentrations are equal to unity, the measured value of the potential-difference of this reaction has been called its "electrolytic potential" (see page 253). Absolute values of the "electrolytic potentials" cannot be obtained with certainty at present. The question now arises whether or not such values may be calculated directly from purely chemical data.

In order to calculate the value of the electrolytic potential, it is only necessary to know the maximum quantity of work obtainable when, by means of a non-electrical, isothermal, reversible process, the substances involved on one side of the reaction equation at unit concentration are transformed into the substances involved on the other, likewise at unit concentration. If now the transformation be imagined to take place electrically, the maximum work obtainable is

$$W_e = v\underline{Q}\pi.$$

Since the maximum quantity of work is, according to the second law of energetics, the same whatever the process used,

$$W_m = W_e = v\underline{Q}\pi,$$

or

$$\pi = \frac{W}{v\underline{Q}}.$$

The value of W can, in the case of gases and dissolved substances in dilute solutions, be calculated.

Consider the system,

$$aA + bB \cdots + v\underline{Q}\,(+) \rightleftarrows dD + eE \cdots$$

[1] Le Blanc, *Ztschr. Electrochem.*, 9, 635 (1903); Abegg-Skukoff, *Ztschr. Electrochem.*, 12, 457 (1906).

in equilibrium, that is to say, under such conditions of concentration that no work is required to carry out the process in either direction. Further, let these concentrations be represented by

$$C_A', C_B', \cdots C_D', C_E', \cdots,$$

and the number of mols of the substances involved by

$$a, b, \cdots d, e, \cdots,$$

respectively (see page 253). Then according to the mass action law, the following relation exists between the quantities of the substances entering the reaction: —

$$\frac{C_A'^{a} \times C_B'^{b} \cdots}{C_D'^{d} \times C_E'^{e} \cdots} = K_c',$$

where K_c' is the equilibrium constant.

In order to calculate the maximum work W of the process, we may proceed as follows: —

1. With the aid of the simple gas laws which apply to dissolved substances (see page 168), the work expended or gained in bringing the given number of mols of the substances on one side of the above reaction equation from the concentration unity to the concentrations C_A', C_B', ··· may be calculated.

2. Under equilibrium conditions, these substances at the above concentrations may be transformed into the substances on the other side of the reaction equation at the concentrations C_D', C_E', ···, without the expenditure of work.

3. Finally, the quantity of work involved when the concentrations of the latter substances are changed from C_D', C_E', ··· to unity may be calculated.

If T is the room temperature and W the maximum work of this process, the following equation is obtained from the above calculations.[1]

$$W = RT \ln K_c'.$$

Therefore the absolute value of the "electrolytic potential" is given by the equation,

$$(\text{EP}) = \frac{RT}{\nu\underline{Q}} \ln K_c'.$$

By combining this equation with that given on page 253, the following general expression is obtained: —

[1] For further particulars see Nernst, *Theoret. Chem.*, 4th edition, p. 630 (1903).

$$\pi \text{ (absolute)} = \frac{RT}{\nu \varrho}\left(\ln \frac{C_A^{a'} \times C_B^{b'} \cdots}{C_D^{d'} \times C_E^{e'}} + \ln \frac{C_D^{d} \times C_E^{e} \cdots}{C_A^{a} \times C_B^{b}}\right)$$

or

$$\pi \text{ (absolute)} = \frac{RT}{\nu \varrho}\left(\ln K_e' + \ln \frac{C_D^{d} \times C_E^{e} \cdots}{C_A^{a} \times C_B^{b} \cdots}\right),$$

where C_A, C_B, $\cdots$ C_D, C_E, $\cdots$ represent any concentrations of the substances involved.

The value of K_e, the equilibrium constant of the single reaction which takes place at one electrode, cannot, however, be experimentally determined, for a chemical reaction always consists of an oxidation and a simultaneous reduction; never of one of them alone. By chemical methods, it is only possible to determine, in a given experiment, the equilibrium constant of the total reaction taking place at the two electrodes. It is, therefore, not possible by means of determinations of equilibrium constants to obtain a knowledge of the values of the potential-differences of single electrodes. However, with the help of such determinations, and a knowledge of the concentrations of the substances reacting at the electrodes, it is possible to calculate the electromotive force of the cell, which is, if the potential-difference between liquids be disregarded, equal to the sum of the two single potential-differences. This may be done with the help of the equation,

$$\pi = \frac{RT}{\nu \varrho}\left(\ln K_e + \ln \frac{C_D^{d} \times C_E^{e} \cdots}{C_A^{a} \times C_B^{b} \cdots}\right),$$

in which K_e is the equilibrium constant of the total reaction taking place in the cell, π is the electromotive force of the entire cell, and the terms after the logarithm sign are the concentrations of the substances which react at the two electrodes respectively.

In this connection it should be remembered that the electromotive force of any galvanic cell may be calculated by a second method with the aid of the heat of reaction Q, and the temperature coefficient of the potential-difference $\frac{d\pi}{dT}$. The equation is that formulated by Helmholtz (see page 173):—

$$\pi = \frac{Q}{\varrho} + T\frac{d\pi}{dT}.$$

The former equation, first put forward by van't Hoff in the year 1886, has recently, at the instance of Bredig, been tested experimentally by Knüpffer.[1] The results obtained will now be considered.

[1] *Ztschr. phys. Chem.*, **26**, 255 (1898); also, *Ztschr. Elektrochem.*, **4**, 544 (1898).

The double reversible chemical transformation,

$$\underset{\text{solid}}{TlCl} + \underset{\text{dissolved}}{KSCN} \rightleftarrows \underset{\text{solid}}{TlSCN} + \underset{\text{dissolved}}{KCl},$$

was investigated. Since the transformation is independent of the quantity of the solid salts, and since the concentrations of the latter may be regarded as constant, it is only necessary to consider the substances in solution. It is, moreover, assumed that the solutions are dilute and that the dissolved substances are completely dissociated, *i.e.* are present in solution in the form of potassium, sulfocyanate, thallium, and chlorine ions. The potassium ions take no part in the reaction. The equilibrium conditions are, then, given by the equation,

$$\frac{C_{Tl^{\cdot}} \times C_{Cl^{'}}}{C_{Tl^{\cdot}} \times C_{SCN^{'}}} = \frac{C_{Cl^{'}}}{C_{SCN^{'}}} = K_c.$$

Attention is called to the fact that

$$C_{Tl^{\cdot}} \times C_{Cl^{'}} = S$$

is the solubility product of a saturated thallium chloride solution, and that

$$C_{Tl^{\cdot}} \times C_{SCN^{'}} = S'$$

is that of a saturated solution of thallium sulfocyanate. Hence the equilibrium constant is in this case equal to the ratio of the two solubility products and may be calculated from these quantities. It was, in fact, determined by ascertaining the concentrations of the chlorine and sulfocyanate ions in solutions formed by shaking a solution of potassium chloride with solid thallium sulfocyanate, and by shaking a solution of potassium sulfocyanate with solid thallium chloride. The following average results were obtained for this reaction:—

Temperature ($t°$)	Equilibrium Constant
0.8°	1.74
20.0°	1.24
39.9°	0.85

Using these values of the equilibrium constant, it is possible to calculate, for any known concentrations of chlorine and sulfocyanate ions, the values of the electromotive force of this process at these temperatures. By placing

$$\frac{C_{Cl}'}{C_{SCN}'} = a$$

in the equation given on page 269, the following expression is obtained: —

$$\pi = \frac{RT}{\mathfrak{Q}}(\ln K_c + \ln\frac{1}{a}) = \frac{RT}{\mathfrak{Q}}\ln\frac{K_c}{a}.$$

In order to be able to measure directly this electromotive force, it is necessary to devise a cell by means of which this reaction may be made to produce an electric current. Such a cell is the following combination: —

Thallium amalgam — KCl solution sat. with TlCl
Thallium amalgam — KSCN solution sat. with TlSCN

If, when this cell is in action, the positive electric current flows in the cell from the upper to the lower thallium amalgam in the above scheme, thallium and sulfocyanate ions are formed while simultaneously thallium and chlorine ions disappear. Hence only the chlorine and sulfocyanate concentrations are changed. The electromotive force of the cell must, therefore, depend upon the ratio of these two concentrations to each other.

The values of the electromotive force found by experiment agree well with those calculated with the aid of the equilibrium constants, as may be seen from the following table: —

Temperature	Electromotive Force	
	Calculated	Found
0.8°	17.1	17.5 millivolts
20.0°	9.8	10.5 millivolts
39.9°	0.6	1.0 millivolt

It may be remarked, further, that this cell can also be considered as a concentration cell in respect to the thallium ions, and that its electromotive force can also be calculated by means of the equation applying to such cells.

One further interesting relation is shown by the equation given above. If a is made equal to K_c, *i.e.* if equilibrium concentrations are maintained, then the electromotive force of the cell is equal to zero. This follows from the fact that, when chemical equilibrium exists in a cell, electrical equilibrium must also exist. Utilizing this fact, the appearance of a state of equilibrium may be shown by electrical measurements. Thus Cohen[1] determined transition points by means of measurements of electromotive force. Zinc sulphate crystallizes at room temperature with seven molecules of

[1] *Ztschr. phys. Chem.*, 14, 53 and 535 (1894).

water, while at a somewhat higher temperature it crystallizes with six molecules. Hence with the combination,

$$Zn - ZnSO_4 \cdot 7\ H_2O \text{ in contact with the solid salt}\text{-------}$$
$$Zn - ZnSO_4 \cdot 6\ H_2O \text{ in contact with solid salt}\text{----------}$$

which is a concentration cell (or in this case a transition cell), an electric current may be obtained because the two hydrates are not equally soluble. Its construction is conditioned by the fact that below the transition temperature the metastable hydrated salt, $ZnSO_4 \cdot 6\ H_2O$, may exist for some time. This condition can, however, be avoided by an artifice. If the temperature of such a cell be varied, so slowly that the solution is always saturated, to the transition temperature, the electromotive force decreases and finally at this temperature becomes equal to zero, since here the solubility curves of the two hydrated salts intersect each other. From what has already been stated in reference to concentration cells, evidently the relations existing in this cell may be calculated.

The reaction,

$$\text{Metal oxide} \rightleftarrows \text{metal} + \text{oxygen},$$

and also the reaction,

$$\text{Metal halide} \rightleftarrows \text{metal} + \text{halogen},$$

forms an especially simple case. Here the following equation holds,

$$W = RT \ln p_d$$

where p_d represents the dissociation tension or pressure of the metal oxide at the temperature T,[1] for it alone determines the equilibrium. In this equation W represents the work obtainable when one mol of oxygen passes from a pressure p_d atmospheres to a pressure of one atmosphere. It may be obtained in the form of electrical energy with the aid of the cell,

Metal — solution of metal oxide (sat.) — oxygen (atm. pressure).

When one mol of oxygen is transformed in this cell, the electrical work,

$$W_e = 4\ \mathrm{F}\Omega.$$

Hence we have the following equation: —

$$\mathrm{F} = \frac{RT}{4\Omega} \ln p_d.$$

[1] Rothmund, *Ztschr. phys. Chem.*, **33**, 69 (1899); and Lewis, *Ztschr. phys. Chem.*, **55**, 449 (1906).

Therefore, the value of E being known, that of p_s may be calculated. This cell may also be considered as a concentration cell in respect to oxygen.

The investigation of Luther and Sammet[1] furnishes an example of a somewhat more complicated relation between the electromotive force and the equilibrium constant. The equilibrium constant of the reaction,

$$6\,H^{\cdot} + IO_3' + 5\,I' \rightleftarrows 3\,I_2 + 3\,H_2O,$$

was determined chemically, giving the following: —

$$K_{c\ (25°)} = \frac{(H^{\cdot})^6 \times (IO_3') \times (I')^5}{(I_2)^3} = 2.8\ (+0.3) \times 10^{-47}.$$

The above reaction may now be considered to be made up of the following individual processes: —

$$2\,IO_3 + 12\,H^{\cdot} + 10\,\mathfrak{Q}\,(-) \rightleftarrows I_2 + 6\,H_2O; \qquad (a)$$

$$I' + 3\,H_2O + 6\,\mathfrak{Q}\,(+) \rightleftarrows IO_3' + 6\,H^{\cdot}; \qquad (b)$$

$$4\,I' + 4\,\mathfrak{Q}\,(+) \rightleftarrows 2\,I_2. \qquad (c)$$

A summation in the usual manner of the members on either side of the $\rightleftarrows$ sign of these equations gives the above original reaction equation.

If now all three processes exist in equilibrium in a mixture, and if a reversible electrode for each process be placed in the mixture, then it follows from what has been said in the last two sections that the three potential-differences between the respective electrodes and the solution must be equal to each other. Under these circumstances these potential-differences will be represented by the following equations: —

$$\underset{\text{electrode}-\text{electrolyte}}{E_{(a)}} = \underset{0}{E_{(a)}} + \frac{RT}{10\,\mathfrak{Q}} \ln \frac{(H^{\cdot})^{12} \times (IO_3')^2}{I_2};$$

$$\underset{\text{electrode}-\text{electrolyte}}{E_{(b)}} = \underset{0}{E_{(b)}} + \frac{RT}{6\,\mathfrak{Q}} \ln \frac{(H^{\cdot})^6 \times (IO_3')}{I};$$

$$\underset{\text{electrode}-\text{electrolyte}}{E_{(c)}} = \underset{0}{E_{(c)}} + \frac{RT}{2\,\mathfrak{Q}} \ln \frac{(I_2)}{(I')^2};$$

[1] *Ztschr. phys. Chem.*, **53**, 641 (1905); *Ztschr. Electrochem.*, **11**, 293 (1905).

and when the potential-differences are equal we obtain the following:—

$$\underset{\sim}{E}_{(b)} - \underset{\sim}{E}_{(a)} = \frac{RT}{30\,\underline{Q}} \ln K;$$

$$\underset{\sim}{E}_{(c)} - \underset{\sim}{E}_{(b)} = \frac{RT}{6\,\underline{Q}} \ln K;$$

$$\underset{\sim}{E}_{(c)} - \underset{\sim}{E}_{(a)} = \frac{RT}{5\,\underline{Q}} \ln K.$$

For process (*a*) it was possible to obtain a reversible platinum electrode. The concentrations of $H^{\cdot}$, IO_3', and I_2 were found to be of considerable magnitude and also measurable. Hence it was possible to determine $\underset{\sim}{E}_0^{(a)}$ and therefore also $\underset{\sim}{E}_0^{(b)}$ and $\underset{\sim}{E}_0^{(c)}$.

In an analogous manner the reaction,

$$6\,H^{\cdot} + BrO_3' + 5\,Br' \rightleftarrows 3\,Br_2 + 3\,H_2O,$$

was investigated. It was found possible to calculate the corresponding values for chlorine. The following results referred to the calomel cell were obtained:—

$\underset{\sim}{E}_0$ electrode ⟵ electrolyte	Iodine	Bromine	Chlorine
Process (*a*)	0.894	1.186	1.25
Process (*b*)	0.802	1.138	1.23
Process (*c*)	0.345	0.812	1.12

In the case of bromine and of iodine there exists a considerable potential-difference between the liquids. By means of an artifice this has been made calculable, thus permitting it to be taken into consideration in calculating the above values. The temperature of the measurements was 25°.

It being known that at the transformation temperature, or, more generally speaking, at the point of equilibrium of two systems, the potential-difference is equal to zero, it may at once be concluded that no potential-difference exists between a solid and a fused metal at its melting point. It is impossible, therefore, to obtain an electric current from a cell composed of an electrolyte, and of a fused and a solid electrode of the same substance at this temperature. From

this it is evident that the heat of fusion, no more than the heat of solution (see also page 227) can be considered exclusively as the direct source of the electrical energy. This conclusion has been confirmed by the results of experiment.[1] If such a cell be placed in surroundings of a temperature other than the melting point, whereby either the liquid or the solid phase must become unstable, naturally an electric current is obtained because the two phases are no longer in equilibrium; but the one is capable of undergoing transformation into the other with the simultaneous production of free energy.

VELOCITY OF IONIZATION. PASSIVITY. CATALYTIC INFLUENCE

Up to the present the velocity of the passage of a substance to and from the ionized state has been left entirely out of consideration under the tacit assumption that, in comparison with the velocities usually measured, it is infinitely great. In the case of the Daniell cell, for example, at a constant temperature, the electromotive force is dependent only on the concentrations of the two solutions. Constant properties are ascribed to the zinc (which furnishes the ions) which are also independent of the strength of the electric current. It may now be questioned whether there are not cases in which the velocity of the formation of ions is no longer infinitely great, but possesses very different values under different circumstances. What would happen in the case of the Daniell cell if suddenly the velocity of the formation of zinc ions should fall to zero? In answer to this question it may be stated that the zinc would then behave like a noble metal and that the cell would no longer of itself furnish an electric current. If, furthermore, with the aid of an independent electromotive force, an electric current should be sent through the cell in the direction of the current of an ordinary Daniell cell, oxygen would be evolved at the zinc electrode.

In general there are a number of possible processes which may take place at an electrode upon the passage of an electric current, and of these processes, *that one takes place which gives rise to the highest electromotive force.* Here again it is assumed that the velocity of ionization is infinitely great. If this velocity is not sufficiently great, the above principle becomes invalid.

It sometimes happens that a base metal which under ordinary circumstances is dissolved as required by its valence and Faraday's law, under other conditions behaves like a noble metal.

[1] *Ztschr. phys. Chem.*, **10**, 459 (1892).

This behavior is called *passivity*. It was first observed with iron at the end of the eighteenth century. In concentrated nitric acid iron loses the power of dissolving with the evolution of hydrogen which it possesses in dilute acids. Even when used as an anode in dilute nitric acid it does not go into solution, but instead permits an evolution of oxygen. Recently it has been found that this phenomenon of passivity is of frequent occurrence, occurring with iron, nickel, and other metals in alkali solutions, with nickel also when it is used as an anode at ordinary temperatures in salt solutions which are neutral, or acid with nitric or sulfuric acid.

Until recently, the phenomena of passivity were explained on the assumption of the existence of a film of oxide covering the metal and protecting it mechanically from corrosion. There is no doubt but that this explanation is a satisfactory one for a large number of cases. This is sometimes evident from the appearance alone. For example, lead when used as an anode in a pure sulfuric or chromic acid solution with a sufficiently small current density is insoluble and becomes covered with a visible layer of lead sulfate or peroxide at which oxygen is evolved. Analogous behavior is always observed when a salt, the anion of which forms a difficultly soluble compound with the anode metal, is used as the electrolyte.

It is a remarkable fact that the anode metal is easily dissolved when, besides a salt of the above description, the electrolyte contains another one in excess which is indifferent and which furnishes an anion which forms an easily soluble salt with the anode metal. This behavior is utilized technically in the preparation of difficultly soluble compounds (Luckow's process).[1] For example, lead, when used as an anode in a solution of sodium chromate and sodium chlorate, dissolves easily, and a beautiful precipitate of lead chromate is formed which rolls from the electrode, leaving it still bright. This is explained by assuming that, due to the action of the indifferent ions in the mixed solution, a liquid layer free from chromate ions is formed directly at the surface of the electrode soon after the electrolysis is started. The adhesion of the precipitate to the electrode is thus prevented. Hence only at the beginning of the electrolysis can a precipitate of lead chromate be formed directly on the anode, and this precipitate does not protect the electrode, for a covering impenetrable to ions can only be formed when it can be continually patched or repaired.

After the above presentation of the subject, it would be justifiable

[1] Le Blanc and Bindschedler, Isenburg, Just; *Ztschr. Elektrochem.*, 8, 255 (1902); 9, 275 and 547 (1903).

for one to expect that, if the passivity of a metal in an electrolyte is governed by the formation of a precipitate, the addition of a second electrolyte in which the same metal as an anode dissolves, forming a soluble compound, would overcome the passivity and cause the solution of the metal with the simultaneous formation of a precipitate which would fall from the electrode, as in the case of the lead chromate.[1] This holds for individual cases, as for example nickel and iron in alkali solutions, but not in others. For instance, although nickel as an anode dissolves in sodium nitrate, upon the addition of sodium chloride no precipitate is formed. It seems scarcely possible to explain this case of passivity in the above manner, *i.e.* on the assumption of the formation on the originally active metal of a protective coating. Some kind of an insoluble oxide or other compound may gradually form. *It cannot, however, be the cause of the passive state of the metal, but, on the other hand, must be the result of previously existing passivity.* The same can be said of a film or coating of a gas which may appear. Up to the present, the optical investigation of the electrode surface has not led to a conclusive result. It would only be of decisive significance if it furnished certain proof that in individual cases of passivity no oxide layer or coating is formed. A proof of the presence of such a coating, on the other hand, could not, as already emphasized, be considered as a conclusive result in the opposite direction.

The above discussion brings us to the idea already indicated, that here we are often dealing with nothing more than the phenomenon of reaction velocity. It is well known that the velocity of a large number of reactions is not only greatly changed by temperature changes, but also by the addition of substances which are apparently inert. Furthermore, it is known that a large number of reactions proceed with such a moderate velocity that they can be easily followed. It should not surprise us especially, therefore, to know that the velocity with which a metal goes from the elementary state to the ionic state is not always very great. This tracing back of real passivity to an exceedingly small ionization velocity of the metal is a gain in that it uncovers the real character of this phenomenon. It is then only a special, if also an especially interesting, case of reaction velocity.[2]

Platinum as an anode does not dissolve in a solution of potassium

[1] Le Blanc and Levi, Boltzmann-Festschrift, 1904, and *Ztschr. Elektrochem.*, 11, 9 (1905).

[2] Less general conceptions of passivity are given by W. Müller, *Ztschr. Elektrochem.*, 11, 755 and 823, and by O. Sackur, in the same volume, p. 841 (1905).

cyanide, but according to F. Glaser,[1] it dissolves like a base metal in the same solution without the aid of the electric current, although very slowly, accompanied by the evolution of hydrogen. This must be considered as a case of true passivity.

The investigations of Hittorf on chromium[2] may be interpreted in a similar manner. According to the choice of solvent, temperature, etc., the chromium is dissolved at the anode in a di-, tri-, or hexavalent state. In dilute hydrochloric acid, for example, the chromium dissolves at moderate temperatures in the divalent state. If, however, solutions of the alkali sulfates be subjected to electrolysis at 100° *t*, using metallic chromium as an anode, chromic acid is obtained. In the former case the process is spontaneous and therefore is capable of doing work. Here the chromium plays, in all respects, the part of a base metal, simulating zinc. In the second case work must be expended in order to bring the chromium into solution. The chromium now behaves like a noble metal. This process especially directs our attention to the fact that *the electromotive force depends, not upon the substance, but upon the process.* Moreover, calculated results can only be correct when the assumed process actually takes place alone. It may be said that in the first case the velocity of the formation of bivalent chromium ions is very great, while in the second case it is so small that the formation of hexavalent ions takes place. Here is an example of a real transmutation, *i.e.* a transformation of a base metal into a noble one, although of a different kind from that sought by the alchemists. At present nothing further is known of the conditions upon which this change in reaction velocity depends.

Analogous relations exist, according to Luther,[3] in the case of ozone. Ozone possesses different electromotive activity and enters a reaction with different valences according to the nature of the indifferent electrode. At a polished platinum anode it is univalent, while at a polished iridium anode it is divalent.

Furthermore, in the case of metals such changes in valence often take place with changes in the anodic treatment. For example, zinc and copper, as anodes, dissolve at least partly in the univalent state in the presence of oxidizing agents. Since these univalent ions are strong reducing agents, the oxidizing agent is reduced or hydrogen is evolved at the anode. Thus we have, as a noteworthy result, a reducing action at the anode.[4]

[1] *Ztschr. Elektrochem.*, 9, 11 (1903). [2] *Ztschr. phys. Chem.*, 25, 729 (1898).
[3] *Ztschr. Elektrochem.*, 11, 832 (1905).
[4] Luther and Schilow, *Ztschr. phys. Chem.*, 46, 777 (1903).

It does not seem impossible that the latter change in valence may be explained in a manner similar to that given on page 267 for the formation of complex compounds when a metal is dissolved. In both cases there may be a continual removal of one kind of ions and thus a tendency to favor the formation of this kind of ions. However, a definite statement of the cause of the phenemenon cannot be given until the subject is further investigated.

In closing this discussion of passivity, a number of cases in which a catalytic influence on an electro-chemical process has been observed will be presented.

From the cell,

$$Zn - ZnSO_4 \text{ solution} - HNO_3 \text{ solution} - Pt,$$

an electromotive force of 0.7 of a volt according to the investigation of Ihle[1] is obtained if the nitric acid solution is dilute and free from nitrous acid. During the action of the cell, hydrogen is evolved at the platinum electrode. If now a small quantity of nitrous acid be added near the platinum, the evolution of hydrogen ceases and simultaneously the electromotive force rises to about one volt.

The explanation is as follows: The nitric acid is an oxidizing agent, *i.e.* it is capable of producing hydroxyl ions by undergoing decomposition into the lower oxides of nitrogen. The velocity of the formation of these ions is, however, under ordinary circumstances practically equal to zero. Hence the nitric acid does not behave like an oxidizing agent, but like any other acid, and therefore causes hydrogen to be evolved at the cathode as usual. The nitrous acid accelerates the formation of the hydroxyl ions, and since this process takes place spontaneously with a much higher electromotive force, it replaces the evolution of hydrogen. Consequently the electromotive force of the cell rises.

Finally, the observations of Förster[2] and Voege[3] on the reduction of potassium chlorate should be mentioned in connection with this subject. The former found that when high-current densities are used, this salt is scarcely at all reduced when the cathode is of platinum, lead, zinc, or nickel, very strongly reduced when the electrodes are of wrought iron, and only moderately when the electrodes are of cobalt. The latter investigator found that in acid solutions the activity of the reduction is dependent upon the material used for the cathode.

[1] *Ztschr. phys. Chem.*, 19, 577 (1896).
[2] *Ztschr. Elektrochem.*, 4, 386 (1897).
[3] *J. Phys. Chem.*, 3, 577 (1899).

It is very remarkable that, according to the choice of cathode metal, reducing action can be made to take place to different stages of the same depolarizer. Thus with the use of mercury as an electrode, Tafel[1] was able to reduce nitric acid quantitatively to hydroxylamine, while with a copper electrode covered with spongy copper he was able to reduce it almost quantitatively to ammonia. If blank copper electrodes are used, a yield of about 15 per cent of hydroxylamine may be obtained. It is evident that observations such as these may become of commercial importance. They will be referred to again at the end of the chapter on electrolysis and polarization.

The influence of the anode material on the course of electrolytic oxidation processes is shown in the use of platinum and lead peroxide as anodes in the electrolytic regeneration of chromic acid. Only when the latter is used is a satisfactory yield obtained. The same difference has been observed in the oxidation of hydriodic to perhydriodic acid. According to E. Müller and Soller[2] both of these cases are examples of the catalytic effect of the cathode material.

Although apparently they do not belong to this discussion, a few observations of Luther[3] will be mentioned. He found that the addition of a small quantity of a dissolved substance which exists in several different states of oxidation to the oxidizing or reducing agent being investigated, is without influence upon the potential-difference, but facilitates its measurement. Thus with the use of platinum electrodes it is difficult to measure the potential-difference of a chromi-chromate solution, evidently because of the slowness of the reaction, —

$$CrO_4'' + 8\,H^{\cdot} + 3\,\ominus(-) \rightleftarrows Cr''' + 4\,H_2O.$$

By the addition of a small quantity of an iron salt, this difficulty is removed. The concentration ratio $\frac{Fe'''}{Fe''}$ becomes so adjusted that the corresponding potential-difference is equal to that of the chromi-chromate solution. Now since the velocity of the reaction

$$Fe'' + \ominus(+) \rightleftarrows Fe'''$$

is comparatively great, the platinum electrode has become to a greater extent unpolarizable. Naturally by means of such an addition it is not possible to obtain a continuous large current of electricity.

From these examples, which might easily be increased, it is suffi-

[1] *Ztschr. anorg. Chem.*, **31**, 289 (1902).
[2] *Ztschr. Elektrochemie*, **11**, 863 (1905).
[3] *Ztschr. phys. Chem.*, **36**, 400 (1901).

ciently evident that catalytic influences which are apparently insignificant produce very considerable effects in electro-chemistry. It is probable that in the future very remarkable discoveries may be made in this little-investigated field.

GENERAL THEORY OF THE COURSE OF THE ELECTRO-CHEMICAL REACTIONS

The idea that possibly the process of evaporation may be explained by the formation of a layer of saturated vapor directly on the surface of the liquid which gradually diffuses into the surroundings, and that the rate of evaporation depends on the rate of this diffusion, was first presented by Stefan.[1] Somewhat later, and apparently without knowledge of Stefan's work, Noyes and Whitney[2] came to an analogous conclusion in studying the velocity of solution of solid bodies. They found that the latter is proportional to the difference in concentration of the saturated solution and that of the solution surrounding the body at the time the velocity of solution was measured.

The theory put forward for these two special cases was generalized by Nernst,[3] and in this form it was endeavored to apply it to all chemical reactions taking place in heterogeneous systems. According to the expanded theory, equilibrium always exists at the boundary surface of two reacting phases, so that the reaction velocity is determined solely by the rate of decrease of the difference between the concentration at the surface and that in the interior of the phase. If now more comprehensible relations be obtained by reducing the thickness of the layer in which the fall in concentration takes place to a certain value l by suitable stirring of the solution, then the velocity of reaction is represented by the equation,

$$U_r = \frac{D_\infty \times s}{l}(C - C'),$$

where D_∞ represents the diffusion coefficient, s the contact surface of the reacting phases, and $C - C'$ the concentration-difference involved. The value of l is dependent on the temperature, the solvent, and the speed of stirring.

From this theory a number of interesting conclusions may be

[1] *Wied. Ann.*, 41, 725 (1890).

[2] *Ztschr. phys. Chem.*, 23, 689 (1897).

[3] *Ztschr. phys. Chem.*, 47, 52; and also Brunner, *Ztschr. phys. Chem.*, 47, 56 (1904).

drawn. The velocity of solution of a rod of benzoic acid in pure water would be for a given surface, temperature, and speed of stirring, proportional to the product of the coefficient of diffusion and the concentration of the saturated solution, *i.e.*

$$U_s = \text{const.} \times D_\infty \times C.$$

In this case C' is equal to zero. If now at the same temperature and the same speed of stirring, a rod of any difficultly soluble oxide or hydroxide, with a surface equal to that of the rod of benzoic acid, be placed in a saturated solution of benzoic acid, then its rate of solution will be equal to that of the rod of benzoic acid in pure water, *i.e.* equal to a const. $\times D_\infty \times C$. This must be so, for there is always at the surface of the solid oxide a layer of liquid saturated with it, *i.e.* a layer of a solution of hydrogen ions of a very small concentration corresponding to the slight solubility of the oxide. The benzoic acid which diffuses to the surface of the oxide is completely neutralized; its concentration is thus reduced practically to zero. Hence the rate of solution of the oxide is governed by the coefficient of diffusion of the benzoic acid D_∞ and the concentration of the saturated solution C (not considering the constant involved).

Plainly nothing essential is changed if a large rod of some base metal such as magnesium be substituted for the rod of oxide. Since the concentration of hydrogen ions at the surface of the metal is very small, it may be considered to be practically equal to zero. The rate of solution of the metal would then depend only on the velocity of diffusion of acid to its surface where hydrogen ions lose their charges, magnesium ions form, and hydrogen gas is evolved. As above indicated, this is true provided all processes which consist in the simple giving up or taking on of electrical charges by a substance at the boundary surface between metallic and electrolytic conductors are like those which consist in mere transition through a boundary surface without electrical change, taking place so rapidly that equilibrium is constantly maintained at the boundary surface. It makes no difference here whether or not the substance goes over into another phase, *i.e.* electrolytic separation and solution, or whether or not one of the substances dissolved in the electrolyte is transformed into another soluble substance, *i.e.* real electrolytic oxidation and reduction.

We may proceed a step farther. If the rod used in the above-cited case be replaced (other conditions remaining the same) by any unattacked electrode of the same form and size, and if a cathode potential be imparted to it such that the concentration of H ions

formed directly at its surface is very small, then the electric current (which can pass only through the discharging of H ions) is equivalent to the quantity of H ions furnished by the diffusion of the acid and the electrolytic transference. The transference of H ions can be eliminated by taking a solution containing a sufficient excess of salt. The velocity of reaction, that is, the current-strength, must then be equal to the velocity of solution of the oxide rod in the same acid solution. Hence after a certain cathode potential is reached, the current-strength remains constant and independent of a further increase of this potential. This holds only within certain limits, *i.e.* until some other process begins also to take place.

Experimental results which have been obtained are in good agreement with this theory.

In the case of all electrolytic reductions and oxidations for which the assumption holds that all reactions coming into consideration are very rapid as compared with the velocity of diffusion, the velocity of diffusion and the kind of stirring are the chief factors influencing the processes at the electrodes.

There are also processes which take place at the electrodes which not only consist in the giving up or taking on of electric charges, but also are accompanied by pure chemical reactions (in a homogeneous system). Such a reaction is the following: —

$$\text{Chinone} \rightleftarrows \text{Hydrochinone.}^{1}$$

According to the discussion on page 267, we must consider that this reaction results from the discharging of hydrogen or hydroxyl ions at the electrode, and the reacting of the gas so formed with the chinone or the hydrochinone, as the case may be. The latter pure chemical reaction, however, proceeds very slowly. In such cases the velocity of reduction of chinone or the velocity of oxidation of hydrochinone is independent of the more rapid process of diffusion and is characteristic of the process in question. It is dependent on the character of the depolarizer. Such slow reactions as the oxidation or reduction reaction just mentioned are often met with in the case of organic substances. With such depolarizers hydrogen or oxygen is evolved at the electrode at a less current density than it is, under otherwise the same conditions, in the case of very active depolarizers.

Even in these latter reactions, it should particularly be noted that it has been assumed that the transference of substances or electrical

[1] Haber and Russ, *Ztschr. phys. Chem.*, 47, 257 (1904).

charges from one phase to another takes place with infinite rapidity. The fundamental assumption of Nernst therefore still remains. Whether or not this assumption is untenable in many cases is still an open question. As far as the process of electrical charging or discharging is concerned, it is probably always rapid, for in homogeneous systems reactions between ions are generally (always?) very rapid. Nevertheless we know of no reason at present why of necessity it must be rapid. There is still less reason for thinking that other processes taking place between phases are generally (or always) rapid. It is known that reactions in homogeneous systems often take place slowly, and no reason is apparent why reactions in heterogeneous systems may not also take place slowly.

It is evident that these questions are most intimately related to the phenomenon of passivity (see page 275). The assumption of a lack of a velocity of ionization made in considering passivity does not necessarily contradict the fundamental assumption of Nernst. It is quite possible that the transition from the metallic to the ionic state may consist, not only of the taking on of an electrical charge, but also of a number of other processes, any one of which by taking place slowly may cause the appearance of the phenomenon of passivity. This latter case is very similar to that of the reaction,

$$\text{Chinone} \rightleftarrows \text{Hydrochinone.}$$

A further explanation must be left to the future.

ELEMENTS POSSESSING DOUBLE NATURES

Although up to the present we have always spoken of substances, like the metals, which can furnish only positive ions, or of substances, like oxygen, which can furnish only negative ions, it is not unreasonable to question whether or not a single substance may possess the power of forming both negative and positive ions. In the year 1900 I stated the following in the second edition of this book. "There are many indications that such cases exist. Thus if a solution of selenous or selenic acid be electrolyzed, a deposition of metallic selenium is obtained at the cathode. This indicates the existence of positively charged selenium ions. On the other hand, a study of hydrogen selenide or sodium selenide leads to the conclusion that selenium also forms negative ions. The behavior of sulfur and of tellurium is similar to that of selenium, and even in the case of the halogens, it is not entirely certain that under all circumstances they form negative ions." In the meantime Walden

has carried out conductivity measurements in solvents other than water which substantiate this view. He[1] found that the conductivity of liquid sulfur dioxide is considerably increased when bromine is dissolved in it, and that of sulfuryl chloride is also increased by the addition of iodine. If now we maintain that the electrical conductance of solutions is due to the presence of ions, then we come to the conclusion that the bromine and iodine in these two solutions dissociates according to the equations, —

$$Br_2 \rightleftarrows Br^{\cdot} + Br';$$

and

$$I_2 \rightleftarrows I^{\cdot} + I'.$$

Closely related to the question of the possibility of an element existing in solution both in the form of positive and of negative ions is that of the possibility of one and the same element going into solution by being electromotively active both as an anode and as a cathode. As a matter of fact, this remarkable behavior is exhibited by tellurium when used in a completely symmetrical arrangement[2] in an alkali solution. At the anode it goes into solution as Te_x'', where x varies between 1 and 2 according to the conditions of experiment, and at the cathode as $Te^{\cdot\cdot\cdot\cdot}$ which unite largely with the OH ions to form the complex ion TeO_3''. This explanation at least seems the simplest one offered up to the present time. Although investigations of other elements have not yet been concluded, they appear to behave in a similar manner.

It is, at all events, of great interest to learn that there is no sudden change between "positive" and "negative" elements, but rather a gradual transition through a number of elements which may be either positive or negative according to circumstances, *i.e.* through elements which possess double natures.

[1] *Ztschr. phys. Chem.*, **42**, 385 (1903).

[2] M. Le Blanc, *Ztschr. Elektrochem.*, 11, 813 (1905); and **12** (Spring of 1906).

CHAPTER VIII

ELECTROLYSIS AND POLARIZATION

THE phenomena observed when an electric current is conducted through an electrolyte between inactive electrodes, as gold, platinum, carbon, etc., will now be considered. It has long been known that the current produces a decomposition of the electrolyte at the electrodes, and that its electromotive force is thereby reduced. The two facts are evidently related. The performance of an amount of work, more or less considerable according to circumstances, is necessary to bring about the decomposition of an electrolyte (as, for example, hydrochloric acid into hydrogen and chlorine), and this work is done by the electric current. When such reduction of the electromotive force occurs, polarization is said to take place. The phenomenon was formerly very little understood, and it is only within the last few decades that its explanation has become possible.

If a current flows for a time through the above-described arrangement, and is then interrupted, the two electrodes being connected through a galvanometer, it will be observed that an electric current, which rapidly becomes weaker, passes between the electrodes in a direction opposite to that of the first or applied current. This is spoken of as the *polarization current*, and its electromotive force is called the *electromotive force of polarization*. From the following it will be evident that this current is derived from the tendency of the materials separated in the neutral condition to return to the ionic condition.

Ohm's law, applied to a circuit possessing a certain primary electromotive force E_1, and containing a "polarization cell," is represented by

$$C = \frac{E_1 - E_2}{R},$$

where E_2 is the electromotive force of polarization, C the current, and R the total resistance of the circuit.

Methods of measuring Polarization.[1] — As already seen, the electro-

[1] For further particulars, see Ostwald-Luther, *Physiko-chemische Messungen*, p. 390.

motive force of polarization is not a constant, but rapidly diminishes when the primary electromotive force is removed; its magnitude is therefore best determined during the passage of the primary current. The accompanying figure represents an arrangement which may be used for the measurement.[1]

One circuit is represented by 1, 2, *a*, 1, and the other by 2, *e*, *b*, *a*, 2; 1 is the source of the electricity, 2 the polarization cell, *e* a compensation electrometer, *b* a known electromotive force, which may be altered at will, and *a* a tuning fork commutator (or, better, a double commutator driven by a motor), which vibrates very rapidly. The arrangement is such that at *a* one circuit is opened and the other simultaneously closed, then the latter opened and the former closed, etc., with each vibration of the tuning fork. The result is practically the same as though both primary and polarization current were independently active. Thus the electromotive force of the latter may be measured under the same conditions as if the primary circuit were continually closed. It is only necessary to alter *b* until the electrometer shows a condition of equilibrium; *b* is then the desired value.

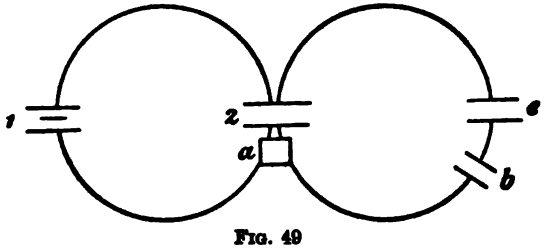


FIG. 49

As the electromotive force of galvanic elements is due to two or more potential-differences, so also in the electromotive force of polarization two single potential-differences are found located at the two electrodes. In order to measure them separately, the method of Fuchs is employed. Its arrangement is shown in Figure 50. A double U-tube is filled with the solution of the electrolyte *e* whose polarization is to be measured. *a* and *b* are two indifferent electrodes connected with the source *Q* of the primary or polarizing current. If the potential-difference at *b* is to be measured, the bent glass tube of the normal electrode *N* (page 246), filled with normal potassium chloride solution, is inserted at *c* in the electrolyte *e*, and *b* is connected with the mercury of the normal electrode by means of the platinum wire of the latter. An element thereby results, consisting

[1] Le Blanc, *Ztschr. phys. Chem.*, **8**, 469 (1890).

of two electrodes and two electrolytes, and the electromotive force of the combination is measured by the usual apparatus at *M*. The potential-difference between *b* and *e* may then be determined by subtraction of the normal electrode potential, and that at the surface of contact between the liquids from the total electromotive force. For determining the potential-difference between *a* and *e* the process is analogous, and using a primary or polarizing current, whose electromotive force gradually increases from zero, it is observed that the electromotive force of polarization is at first very nearly equivalent to that of the primary current. As the latter becomes higher the former falls gradually away from it in magnitude, nevertheless always increasing to some extent. The much-sought-after maximum of polarization does not actually exist.

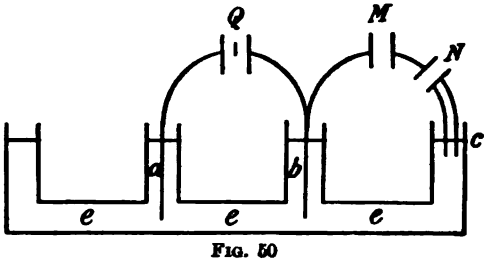


FIG. 50

Decomposition Values of the Electromotive Force. The Hydrogen-Oxygen Cell. Primary and Secondary Decomposition of Water. — There is another characteristic point for the different electrolytes. A continuous current flows and a continuous decomposition only takes place when the electromotive force exceeds a certain value. If an electromotive force less than the above be impressed, only an instantaneous passage of electricity takes place, which may be made evident by inserting a galvanometer into the circuit. The needle of the galvanometer is at first deflected, but returns very nearly to its original position (the effect of secondary disturbing influences will be considered later). This does not happen when the applied electromotive force has reached the value in question.

A better view of these relations may be obtained by plotting the current on the ordinate and the corresponding electromotive force on the abscissa of a coördinate system. The curves thus obtained (see later, Figure 51) all show a more or less abrupt turning point at which the curve changes its direction.[1]

[1] As has already been indicated, the potential-fall due to the resistance of the electrolyte must either be avoided or taken into consideration in the calculations.

Le Blanc determined the magnitudes of these *decomposition values* for a great many electrolytes, chiefly in normal solutions. They may be very exactly determined for salts from which a metal is precipitated by the current, but for other salts, as well as for acids and alkalies, they are less easily found. The following decomposition values were found for salts from which the metal is deposited.[1]

$ZnSO_4$	= 2.35 volts	$Cd(NO_3)_2$	= 1.98 volts
$ZnBr_2$	= 1.80 volts	$CdSO_4$	= 2.03 volts
$NiSO_4$	= 2.09 volts	$CdCl_2$	= 1.88 volts
$NiCl_2$	= 1.85 volts		
$Pb(NO_3)_2$	= 1.52 volts	$CoSO_4$	= 1.92 volts
$AgNO_3$	= 0.70 volt	$CoCl_2$	= 1.78 volts

The decomposition values for sulfates and nitrates of the same metal, as shown by the experiments with cadmium salts and other experiments with the alkalies, are nearly equal. As is evident, the values for the various metals are different. The conclusion to be drawn from the corresponding values for the acids and bases is that there exists a maximum decomposition point, which is exhibited by most of the compounds and exceeded by none. This is about 1.67 volts. Among the acids, however, several gave values below this maximum. The following tables contain the values for acids and bases: —

Acids

Sulfuric	= 1.67 volts
Nitric	= 1.69 volts
Phosphoric	= 1.70 volts
Monochloracetic	= 1.72 volts
Dichloracetic	= 1.66 volts
Malonic	= 1.69 volts
Perchloric	= 1.65 volts
Dextrotartaric	= 1.62 volts
Pyrotartaric	= 1.57 volts
Trichloracetic	= 1.51 volts
Hydrochloric	= 1.31 volts
Hydrazoic	= 1.29 volts
Oxalic	= 0.95 volt
Hydrobromic	= 0.94 volt
Hydriodic	= 0.52 volt

[1] *Ztschr. phys. Chem.*, 8, 299 (1891).

Bases

Sodium hydrate	= 1.69 volts
Potassium hydrate	= 1.67 volts
Ammonium hydrate	= 1.74 volts
¼ n. Methylamine	= 1.75 volts
½ n. Diethylamine	= 1.68 volts
⅛ n. Tetramethyl ammonium hydrate .	= 1.74 volts

The alkali and alkali earth salts of the highly dissociated acids with maximum decomposition values, as sulfates and nitrates, have nearly the same decomposition point, *i.e.* about 2.20 volts. The chlorides, bromides, and iodides have lower values, independent of the nature of the alkali metal. Additivity is exhibited, owing to the mutual independence of the potential-differences produced at the two electrodes. Differences between the values for the various halogen compounds of the alkalies, hydrogen, and the metals are nearly equal; for example, the difference between hydrochloric and hydrobromic acid is the same as that between sodium chloride and sodium bromide.

The salt of a slightly dissociated acid, as sodium acetate, or of a slightly dissociated base, as ammonium sulfate, always exhibits a lower value than that of a highly dissociated acid or base, providing the acid and base possess the maximum decomposition value. The halogen salts of ammonium have lower decomposition values than the corresponding salts of the alkalies; and, in fact, the differences between corresponding salts are equal.

Concerning the effect of dilution in the case of bases and acids which on electrical decomposition evolved oxygen and hydrogen at the electrode, the decomposition values are independent of the dilution, and this is true for all the acids excepting those whose decomposition values are below the maximum. For these, the value rises with increasing dilution, and finally reaches the maximum. This is very marked in the case of hydrochloric acid.

Concentration	Decomposition Point
¼ Normal hydrochloric acid	1.26 volts
½ Normal hydrochloric acid	1.34 volts
1 Normal hydrochloric acid	1.41 volts
1/10 Normal hydrochloric acid	1.62 volts
1/32 Normal hydrochloric acid	1.69 volts

It is also worthy of note that when the maximum value is reached, the acid solution is no longer decomposed into chlorine and hydrogen, but into hydrogen and oxygen.

The above experiments were carried out with platinum electrodes. If other electrodes be used, as gold or carbon, different numerical values are obtained, but the general relations between them remain unaltered.

In order to obtain a better insight into polarization phenomena Le Blanc[1] investigated the potential-difference at the electrode where the metal is electrolytically deposited (the cathode), when the electromotive force of the primary current is gradually increased from zero. He found that the potential-difference at the decomposition point is equal to that which the precipitating metal would itself exhibit in the solution. For example, a normal solution of cadmium sulfate was decomposed at a primary electromotive force of 2.03 volts. The potential-difference of the electrode where the cadmium separated was, —

$$E_{\text{electrode - electrolyte}} = -0.72.$$

Metallic cadmium placed in the solution also gave -0.72 volt. In many solutions the electrode exhibited the potential-difference due to the separating metal before the decomposition point of the solution is reached. For instance, in silver nitrate the electrode had the value of pure silver in silver nitrate even below the decomposition point (0.70). This is due to the great tendency of the silver ions to separate as electrically neutral metal.

It was also possible to demonstrate that the material of the indifferent electrodes, providing no alloy is formed,[2] is without influence upon the magnitude of these potential-differences. The results were the same whether gold, platinum, carbon, or any other metal more positive than that in solution was used. From this it is evident that the electrode itself possesses no "specific attraction" for the electricity, as formerly was imagined.

The process of precipitation and solution of the metals is, therefore, to be considered as reversible. It may be represented as follows: If an indifferent electrode be placed in the solution of a salt of a metal, a very small quantity of the ions leave the ionized state and deposit upon the electrode in the metallic form. This process goes on until the tendency of the ions to deposit in the metallic state is exactly compensated by the electrostatic attraction which exists between the positively charged electrode and the negatively charged

[1] *Ztschr. phys. Chem.*, **12**, 333 (1893).

[2] For further particulars, see Coehn and Dannenberg, *Ztschr. phys. Chem.*, **33**, 609, 1901.

solution. The quantity of ions deposited is, therefore, dependent upon the tendency of the ions to persist in the ionized state. Up to the present we have always spoken of the tendency of the metal to pass into the ionized state. Now we will speak, as naturally we may with equal right, of the tendency of the ions to remain as such. To express this exertion of the ions to hold their electrical charges, the expression *holding power* (Haftintensität) is often used. Numerically this holding power is equal to the electromotive force which is required to deposit an ion in the neutral state.

A certain potential-difference must, therefore, exist at the electrode, there being some metal upon it and the corresponding ions in the solution. The magnitude of this potential-difference need not be, and almost never is, the same as found when the massive metal is in contact with the solution, for the metal deposited upon the electrode does not reach the concentration of the massive metal. The conclusion seems strange at first, for it is customary to consider the concentration of a metal as unalterable. This is only the case above a definite limit. If the metal is not present, at least to the extent of a molecular layer, it does not act as the massive metal. This has been shown by Oberbeck[1] and Königsberger and Müller.[2] When the metal of a salt solution was precipitated upon a platinum plate, the latter exhibited in the corresponding metal solutions the potential-difference characteristic of the massive metal as soon as a certain amount had been deposited. Below this point the electrode exhibited smaller potential-differences corresponding to the lower concentrations of the metal. This fact need not be surprising when it is recalled that gases and dissolved substances have solution pressures dependent upon their concentration.

If the source of an electromotive force be connected with the electrode in such a manner as to tend to separate a metal from the solution, it works against the electrostatic attraction, and more ions can separate as metal. The concentration of the metal upon the electrode is thereby increased, and consequently also its solution pressure P, which tends to prevent a further deposition of the metal, and soon entirely prevents it. To deposit more metal it is necessary to impress a still greater potential-difference. This continues until the maximum concentration of the metal is reached — that is, until the electrode acts as the massive metal. A continual deposition may then take place without further increase of the applied electromotive force, providing, naturally, that the osmotic pres-

[1] *Wied. Ann.*, 31, 336 (1887).
[2] *Phys. Ztschr.*, 6, 847 and 849 (1905).

sure of the ions P remain unaltered. When strong currents are used P does not remain constant, but gradually diminishes, and consequently the potential-difference at the electrode increases.

It must be observed that the separation of positive ions at one electrode as neutral substance is necessarily accompanied by the simultaneous deposition of the corresponding amount of negative ions at the other. Considerations analogous to the above evidently apply to the negative electrode. If, for example, oxygen is set free, the concentration of the gas gradually increases; and, when the solution is saturated, has its greatest value, and consequently also its maximum solution pressure (which opposes the further decomposition of the electrolyte). If more separates, it escapes into the air. It will now be understood why a certain electromotive force is necessary to induce continuous decomposition in an electrolyte; this only occurs when the concentrations of the two substances separating at the electrodes have reached their maximum values. It is also evident that the electrodes upon which metals are deposited should exhibit the potential characteristic of the massive metal when the decomposition point is reached. But it is evidently unnecessary that these maxima of concentration for both electrodes should be reached *simultaneously;* it may sometimes be reached at an electrode before the decomposition point of the solution can be attained, as is the case with a silver solution. The decomposition point of normal silver nitrate is 0.70 volt, but the potential-difference at the electrode upon which silver is deposited is of the same magnitude as that between massive silver and the solution long before this decomposition value is reached.

The polarization due to metal ions having been considered, attention will now be directed to the phenomena presented when gaseous or dissolved substances are separated. These are somewhat more complicated, and have greatly increased the difficulty of understanding the process of polarization. As a simple case, the following cell will be considered: —

Pt (platinized) in hydrogen — water (with a dissolved electrolyte, such as H_2SO_4)----|
Pt (platinized) in oxygen----------|

Consider the two gases to be under atmospheric pressure.

The cell at 17° has an electromotive force of about one volt, and is, as was first shown by Le Blanc, to be considered reversible for small current densities. If an equal opposing electromotive force be connected with this cell, a condition of equilibrium exists; when

a lower electromotive force is applied, water is produced by the oxygen and hydrogen of the cell, and when the electromotive force of the opposing current is greater, water is decomposed. Smale[1] calculated the temperature coefficient of this cell from the Helmholtz formula, using the known heat of formation of water under constant pressure (67,534 cal. at 17°) and the measured electromotive force as data: —

$$\mathrm{F}2 - Q = 2T\frac{d\mathrm{F}}{dT};$$

$$96540 \times 1.07 - 33767 \times 4.189 = 2T\frac{d\mathrm{F}}{dT};$$

$$-\frac{38152}{96540 \times 290} = \frac{d\mathrm{F}}{dT};$$

$$\frac{d\mathrm{F}}{dT} = -0.00136.$$

Q is $\frac{67534}{2}$, since the heat effect corresponding to one equivalent of the substance is employed. Experimental determinations gave as a mean value between 0° and 68°, 0.00141, and between 0° and 100°, 0.00143 (obtained later by L. Glaser), which is a satisfactory agreement with the calculated value.

It has recently been shown[2] that the electromotive force of the hydrogen-oxygen cell at atmospheric pressure and room temperature must be 1.22 volts, a value which is considerably higher than that obtained by earlier investigators, who, perhaps because of the formation of oxides, never succeeded in completely saturating the oxygen electrode. The highest value which has been found is 1.14 volts. This change in the value of the electromotive force of the cell has, however, no influence upon the above calculation, because the cell is capable of producing work reversibly, whatever the pressures of the gases.

Furthermore, at high temperatures, the agreement between the value of the electromotive force calculated from thermodynamical considerations and that found experimentally is very satisfactory.[3]

It may now be predicted that if the hydrogen and oxygen, instead of being at atmospheric pressure, be at a lower pressure, the electromotive force of the cell will be lower. In fact, if the pressures of the gases be reduced almost to zero, the electromotive force will nearly disappear. Under such a condition water may evidently be

[1] *Ztschr. phys. Chem.*, **14**, 577 (1894).

[2] See, for example, *Ztschr. phys. Chem.*, **55**, 473 (1906).

[3] Haber, *Ztschr. Elektrochemie*, **12**, 415 (1906).

decomposed by currents of minimum electromotive force, it being only necessary to apply one which exceeds that of the cell itself by a very small amount. From this it is clear that the electrical energy obtainable through the formation of water from oxygen and hydrogen, or necessary for its decomposition (the two being equal and of opposite sign), may assume any magnitude from zero to a certain value dependent on the pressures of the gases or their concentrations. The heats of formation at constant pressure, on the other hand, are independent of the pressure, within such limits as the gas laws hold. This is the most direct evidence that a simple relation cannot exist between the heat of reaction and the electrical energy obtained. It is, however, possible in this case to calculate the amount of one of these two forms of energy from a knowledge of the other when the changes of the temperature coefficient due to pressure changes are known.

That water may thus be decomposed by minimum quantities of electrical energy seems at first a contradiction of the law of the conservation of energy. This is, however, in no wise the case. The law referred to declares that by the reversible changes of a system from one condition to another, the same amount of work must always be done, and this condition exists in the present case. The decomposition of water into hydrogen and oxygen at atmospheric pressure may be accomplished, on the one hand, by the application of electrical energy alone. A gas cell such as described, the gases being under atmospheric pressure, may be used, an opposing electromotive force just exceeding that of the cell being connected with it. Electrical energy alone then causes the decomposition of the water into hydrogen and oxygen at atmospheric pressure. This same result may, however, be brought about in another way. For instance, a hydrogen-oxygen cell in which the pressure of the gases is one tenth atmosphere may be employed. The electromotive force of this cell being lower than the previous one, less electrical energy is required to produce the hydrogen and oxygen at the reduced pressure. But the work which corresponds to the difference between the two quantities of electrical energy employed must exactly suffice to compress the gases produced at one tenth atmosphere to the pressure of one atmosphere, and thus the total work in the two cases, although done in different ways, has remained the same.

When platinized electrodes are used, the formation and the decomposition of the water are reversible. At atmospheric pressure water may be decomposed by an electromotive force of 1.22 volts. If the electrodes are not platinized, the electrolysis does not take place until the

electromotive force is 1.67 volts. This is the maximum value for decomposition found for the acids and bases, hydrogen and oxygen being the products. It was long considered surprising that the decomposition point in the latter case is so high, notwithstanding the fact that only the partial pressure of the atmosphere is exerted upon each of the gases. Furthermore, the fact that the decomposition point is dependent upon the nature of the indifferent electrode appeared curious.

These results can now be understood. In the first place, when electrodes such as ordinary platinum or gold[1] are employed, the process is no longer a reversible one. These electrodes have too feeble absorbing power to remove the gases as rapidly as they are formed. With platinized electrodes there is equilibrium between the gas dissolved in the solution, that dissolved in or taken up by the electrode, and the volume of gas surrounding the electrode. If the applied electromotive force be great enough to overcome that of the gas cell, gas separates at the electrodes, and thereby its concentration in the solution as well as in the electrode is increased. The former condition of equilibrium is soon reproduced, for the electrode yields its excess of gas to the space about it (which is considered so great that no change in the concentration of this gas in it is produced), and in this manner prevents supersaturation of the liquid. The gas formed by continued decomposition of the electrolyte thus always escapes into a space filled with a gas at constant concentration. The generation can therefore always take place under the same electromotive force.

The conditions are entirely different when the electrodes are of gold or of unplatinized platinum. These have practically no absorbent action on the gases, and there is thus no medium to bring about equilibrium between the solutions of the gases as formed in the cell and the gases in the space about the electrodes. Proceeding on this assumption, the result of a gradually increasing electromotive force

[1] If carbon be used as an electrode, the kind of carbon is an important factor. Carbon is capable of taking up gases to a considerable extent, and this property increases its value as positive electrode of a galvanic element. In the Leclanché element, for example, hydrogen is evolved at the carbon pole, and the property of carbon just mentioned causes the gas to pass quickly from the liquid to the air, thus reducing the polarization at this electrode. For long-continued activity of the cell, the carbon is often incapable of removing the hydrogen with sufficient rapidity, and polarization is the result. If the action of the cell be stopped for a time, the hydrogen dissolved in the liquid has an opportunity to escape, and the element, becoming thus depolarized, again exhibits its original electromotive force, *i.e.* it recuperates.

opposing such a gas cell would be exactly as observed. Beginning with a low electromotive force, a scarcely perceptible decomposition of water would take place, the concentrations of the hydrogen and oxygen in the water being at first inconsiderable. At each subsequent increase of the applied electromotive force so much water at the most may be decomposed that the concentration of the gases in solution at the electrodes is made exactly that which would produce an equivalent electromotive force with platinized electrodes. A higher concentration of the gases can evidently not be produced, otherwise perpetual motion would be possible. This explains the temporary current observed in the galvanometer. Diffusion alone causes disturbances, the gases being thereby very slowly removed from the electrodes and the concentration reduced so that further decomposition takes place. The galvanometer corroborates this, since, after the first deflection, the needle does not return quite to its former position. It thus indicates a slight residual current.[1] Upon gradually increasing the electromotive force, the concentration of the separated gases continually increases, until finally a point is reached at which gas is evolved. The resistance which opposes the formation of bubbles, or another passive resistance of an unknown nature which opposes the escape of the gas into the space above, is then overcome. When this point has been reached, water may be decomposed without causing a further increase in the concentration of the gases dissolved at or in the electrodes. The gases are then continually evolved as bubbles, and the so-called *decomposition point* is observed, that is, *that point above which water may be continually decomposed without the aid of diffusion.* The less the diffusion of separated substance from the immediate neighborhood of the electrode, the more marked is the decomposition point, and indeed often (in the case of metals) the galvanometer exhibits a clearly defined sudden rise in the strength of the current at this point.

However, even this conception does not embrace all actual relationships. It has been observed that the decomposition point is not always identical with the point at which bubbles of gas are formed. The latter point, the observation of which is to a large degree subject to chance, very often is later than the former. Finally, it has been proven that the decomposition point is independent of the pressure.[2] It must then be assumed that, at the decomposition point, the metal is saturated with gas to such an extent that it gives the gas off to the surrounding liquid as rapidly as it is brought up to

[1] Nernst and Merriam, *Ztschr. phys. Chem.*, **53**, 235 (1905).
[2] Wulf, *Ztschr. phys. Chem.*, **48**, 87 (1904).

the metal by a further increase of the electromotive force. This process, which takes place without involving a change in volume, is independent of pressure. From this, the degree of the dependence of the decomposition point on the solubility of the separated gas in the electrode is very evident. It is also evident that the greater the solubility of the gas in the liquid, the farther apart will be the decomposition point and the point at which bubbles appear. This conclusion is confirmed by experience.

The great influence of the electrode material is shown by the investigations of Coehn and Dannenberg,[1] and Caspari.[2] The former two investigators determined the decomposition points at cathodes of various metals, for the most part, in a normal solution of sulfuric acid. If the potential-difference at the reversible platinized platinum electrode be placed equal to zero, the results obtained by them are as follows: —

Metal	Decomposition Voltage ($E_{\text{electrode—electrolyte}}$)
Palladium	+ 0.26 volt
Platinum	— 0.00 volt
Iron	— 0.03 volt
Gold	— 0.05 volt
Silver	— 0.07 volt
Nickel	— 0.14 volt
Copper	— 0.19 volt
Aluminium	— 0.27 volt
Lead	— 0.36 volt
Mercury	— 0.44 volt

Only in the case of palladium is the separation of hydrogen facilitated, and this is most certainly due to the formation of an alloy. In all the other cases, a considerable retardation or hindrance of the separation, or in other words a considerable *over-voltage*, exists. This over-voltage appears to be greatest in the case of metals which possess the smallest occlusion capacity.

In the case of the cathodic polarization of metals in a solution of potassium hydroxide it was found that the order of, and the differences between, the decomposition voltages are the same as those given above. From this it is to be concluded that no alkali-alloy is formed at the decomposition point, but only a separation of hydrogen takes place. Mercury at no time left its place in the above order, and

[1] *Ztschr. phys. Chem.*, **38**, 609 (1901).
[2] *Ztschr. phys. Chem.*, **30**, 89 (1899).

only when high potential-differences are reached is the phenomenon of disintegration or powdering of the cathode, as in the case of tin and lead, which was studied by Haber, Sack,[1] and Bredig, observable. This behavior of tin and lead is explained on the assumption of the formation of an alkali alloy.

If, as in Caspari's work, the electromotive force which is required to produce a visible evolution of gas be determined, the values will be found to be somewhat greater but in the same order as those in the above table. His highest values, obtained with zinc and mercury, are — 0.70 and — 0.76 volt, respectively.

These values are of interest in connection with the chemical solution of metals in acids. It may be seen from the table given on page 248 that zinc tends to separate from a normal solution of hydrogen ions with an intensity of 0.80 of a volt. Therefore, since the over-voltage is equal to 0.70 of a volt, zinc dissolves in a solution which is normal in respect to the hydrogen and zinc ions only very slowly. By increasing the concentration of the zinc ions, as, for example, by the addition of zinc sulphate, the solution of the zinc may be made even slower or brought to a standstill, while by increasing the concentration of the hydrogen ions, or, what is the same thing, of the acid, the action may be accelerated.

Commercial zinc possesses a smaller over-voltage, and therefore is more easily dissolved than is pure zinc. If it be amalgamated, it dissolves less easily and its over-voltage increases; while if pure zinc be amalgamated, the ease with which it dissolves and its over-voltage do not suffer any considerable change.

Not only in the case of hydrogen, but also in that of oxygen, an over-voltage which varies with the nature of the electrode (in this case the anode) is produced by the separation of the gas. Coehn and Osaka,[2] making use of a normal solution of potassium hydroxide as an electrolyte, measured the anode voltage against a constant hydrogen electrode which was also in contact with a normal solution of potassium hydroxide. The values obtained by them are given in the table on the following page.

It should be noted that the decomposition point in this case is identical with that at which visible evolution of oxygen takes place and that the order of the metals is quite different from that in the case of the hydrogen. The results given here indicate that the commercial decomposition of water could be carried out with the least expenditure of energy with the use of nickel electrodes.

[1] *Ztschr. anorg. Chem.*, **34**, 286 (1903).
[2] *Ztschr. anorg. Chem.*, **34**, 86 (1903).

Metal	Decomposition Voltage
Gold	1.75
Platinum (polished)	1.67
Palladium	1.65
Cadmium	1.65
Silver	1.63
Lead	1.53
Copper	1.48
Iron	1.47
Platinum (platinized)	1.47
Cobalt	1.36
Nickel (blank)	1.35
Nickel (spongy)	1.28

Even with the same substance used as an anode the decomposition value varies with the treatment to which the substance has been subjected, *i.e.* with its previous history. This was mentioned on page 296 in reference to carbon. This subject will be further considered later on.

Both bromine and iodine separate reversibly at platinum anodes.

It may be questioned whether the order of the over-voltages obtained under practically zero-current conditions is the same as the order which is obtained during electrolysis with a high current density. Furthermore, is the latter series of values noticeably higher than the former? These questions have been investigated by Tafel.[1] The maximum values thus far obtained are given in the following table. They were obtained at 12° in a 2-normal sulfuric acid

Metal	Over-voltages ($\underline{F}a$)
Mercury	1.30
Lead (polished)	1.30
Lead (rough)	1.23
Cadmium	1.22
Tin	1.15
Bismuth	1.00
Gold	0.95
Silver	0.93 ?
Copper	0.79
Nickel	0.74
Platinum (platinized)	0.07

[1] *Ztschr. phys. Chem.*, **50**, 712 (1905). The change in potential due to the change in the concentration of H ions at the electrodes is, as the experiments with platinized platinums show, negligible.

solution with a current density maintained constant at 0.1 of an ampere per square centimeter of electrode surface. The anode section was separated from the cathode section.

It should be noted that the value of the over-voltage for a given current density is for many metals dependent on the previous treatment to which the electrode has been subjected, as for example, upon the current density maintained when the cathode was previously polarized. The over-voltage of all metals changes slowly as time passes. This change and the dependence of the potential on specific influences is not the same for different metals. An access of the anode solution to the cathode compartment generally lowers the potential-difference. The maximum value of the potential-difference is reached at once with mercury and lead, but very slowly with copper, nickel, and gold, and not at all with polished platinum. The potential decreases with increasing temperature.

The investigations of Förster and Müller,[1] and Förster and Piguet,[2] of anode potentials in 2-normal potassium hydroxide show relationships similar to the above.

Finally, it should be mentioned that E. Müller[3] has found that the over-voltage at the anode, in the case of platinum, is greatly increased by the addition of fluorine ions. It follows from this fact and also from the above-mentioned work of Tafel that the over-voltage depends also on the nature of the electrolyte.

According to the explanations already given, the electromotive force of the hydrogen-oxygen cell is dependent upon the concentrations of the gases, but nearly independent of the nature of the electrolyte. The electrolyte may almost equally well be an acid or a base. The electromotive force is the sum of the potential-differences produced at the hydrogen and oxygen electrodes. That of the former is dependent upon the concentration of the hydrogen ions, that of the latter upon the concentration of the hydroxyl ions, for a given concentration of the gases. According to the law of mass action, the product of the concentrations of the hydrogen and hydroxyl ions is (nearly) always constant without regard to other substances present; therefore, although the values of the single potential-differences may vary considerably on changing the homogeneous solution, their sum always remains the same.[4]

Leaving out of account metal salt solutions reducible by hydrogen,

[1] *Ztschr. Elektrochem.*, **8**, 527 (1902).
[2] *Ztschr. Elektrochem.*, **10**, 714 (1904).
[3] *Ztschr. Elektrochem.*, **10**, 758 (1904).
[4] For further particulars see L. Glaser, *Ztschr. Electrochem.*, **4**, 355 (1898).

and chlorides, bromides, iodides, etc., reducible by oxygen, the ions of water alone take part in the decomposition, instead of those of the dissolved electrolyte, so that with the limitations given, the principle may be expressed: *In electrolysis a primary decomposition of the water takes place.* The actual electrical conductance is brought about by all the ions in the solution, but at the electrode that action takes place which proceeds most easily, and this is usually the separation of the hydrogen and hydroxyl ions. When, for example, a solution of potassium sulphate is being electrolyzed, and the current is not too strong, there is no reason for assuming the separation of potassium and the SO_4 radical at the electrodes, and the subsequent or secondary action of these upon the water. The fact that every acid and base, in so far as they do not possess a lower decomposition voltage, decomposes at 1.67 volts can scarcely be otherwise explained than by the assumption that in every case the same process takes place. If a secondary action, *i.e.* a separation of the radicals at the electrodes and a subsequent reaction of these with the water, takes place, it would be expected that the decomposition point would not be the same in all cases but would vary with the velocity of the action. In the case of acetic acid, for example, a higher potential would be expected, since during electrolysis of it with a strong current only a small quantity of oxygen is found mixed with the gas evolved at the anode. The reaction,

$$4\,CH_3COO' + 2\,H_2O = 4\,CH_3COOH + O_2$$

must therefore take place slowly. Whether or not a primary decomposition of water takes place when strong currents are used evidently depends, for a given concentration, on the velocity of the formation of hydrogen and hydroxyl ions from undissociated water. This subject will be touched upon again.

It should be emphasized that the assumption, made earlier, that the ions carried to the electrode by the electric current always separate on the electrode directly and then react with water or other substances does not appear to be in agreement with facts. That the conduction of the electric current and the decomposition of the electrolyte at the electrodes are not as closely related as was formerly supposed is evident from the simple fact that during the electrolysis of every electrolyte more ions are separated at each electrode than are brought to it by migration (see page 67). Hence in every case some of the ions originally in the solution near the electrodes which have not taken part in the conduction of the current are deposited.

The following conception, which has already been mentioned briefly, appears to me to be decidedly preferable to that formerly accepted. The conduction of the electric current and the chemical changes or separations at the electrodes are not closely related. *All of the ions in the solution take part in the conduction of the electric current, but only those ions the separation of which require the least expenditure of work or energy are deposited or separated at the electrodes.* Thus it may happen that ions which conduct scarcely a measurable part of the current play the most important part in the chemical decompositions at the electrodes, in so far as they are formed with sufficient rapidity.

The following example is well adapted to show the greater simplicity of the newer conception. Suppose that a fairly concentrated solution of a mixture of potassium, cadmium, copper, and silver salts be electrolyzed with a moderate current between platinum electrodes. In conducting the electric current, potassium, cadmium, hydrogen, copper, and silver ions migrate to the cathode. At the cathode, from actual experiment, it is known that the silver is first deposited. This deposition goes on until the number of silver ions remaining is no longer sufficient for the current density maintained, when the copper begins to separate in the same manner. Following copper, cadmium, and finally hydrogen, is deposited. Is not the simplest conceivable explanation of these experimental results that given in the following statement?

Those ions separate first which give up their electric charges most easily. The other ions must wait their turn in the order of their ease of deposition. The process takes place smoothly and comprehensively.

The other conception may now be applied to the same process. According to this conception, potassium, cadmium, hydrogen, copper, and silver ions separate simultaneously at the cathode. The potassium may then set free hydrogen from the water, cadmium from the cadmium salt, copper from the copper salt, and silver from the silver salt. This must be considered to take place, for the assumption cannot well be made that there is always a particle of silver ready to be precipitated in the immediate vicinity of each particle of potassium. The potassium must then separate those ions of whatever kind which happen to be in its vicinity. Of these substances separated by the potassium, the hydrogen sets free cadmium from the cadmium salt, copper from the copper salt, and silver from the silver salt. Of this group of separated metals, the cadmium may set free copper from the copper salt, and silver from the silver salt. Finally, the copper sets free, or deposits, silver from the silver salt. The

final result of all this is that as long as sufficient silver is present, it alone is deposited permanently on the cathode. This conception of the process of electrolysis certainly cannot be said to be as simple as the one given above, and it involves the assumption of all these secondary reactions which no one has ever observed. The question at once arises, why make this complicated assumption when, as has been shown, it can, with greater simplicity, be avoided?

After this discussion, the values obtained during the determination of the decomposition voltage with the use of platinized platinum electrodes is easily understood. Those substances which decompose water will be considered first. Both acids and bases must have the same value, since, as already stated, the product of the concentrations of the hydrogen and hydroxyl ions at the electrodes, and consequently the sum of the potential-differences at the electrodes, is the same in the two cases. In the case of salts, higher values should be obtained, since at the cathode a base is formed whereby the concentration of the hydroxyl ions is greatly increased, with the consequent driving back of the concentration of the hydrogen ions and increase of the potential-difference. A similar line of reasoning holds for the anode at which acid is formed, increasing the concentration of the hydrogen and decreasing that of the hydroxyl ions. The less the dissociation of the acid or base formed, the less the increase in the potential-difference. This has been observed to be the case.

Since that ion is always separated at the electrode which requires the least electromotive force for its separation, no ions other than hydrogen and hydroxyl ions (providing the concentrations of the latter are sufficiently great) come into consideration except when the electromotive force required for their separation is less than that required for the separation of hydrogen and hydroxyl ions. For this reason, the decomposition voltage of the halogen acids, etc., which do not cause a separation of oxygen is lower than that of those acids which do cause the separation of oxygen. Furthermore, while in the case of acids and bases which are decomposed with the separation of hydrogen and oxygen, the decomposition voltage is independent of the concentration (since the product of the concentrations of the hydrogen and hydroxyl ions remains the same), in the case of the halogen acids the decomposition voltage rises with decreasing concentration, since an increase in the concentration of the hydroxyl ions takes place corresponding to the decrease in that of the hydrogen and of the halogen ions. A dilution is finally reached at which oxygen is continuously evolved more easily than is the halogen. At

this dilution, the decomposition voltage is equal to that of water. Such a case has been realized with hydrochloric acid.

In the foregoing pages the current-voltage curve of any electrolyte has always been discussed as if there existed but a single decomposition value which, by means of measurements with an auxiliary electrode, can be divided into an anode and a cathode potential-difference. The recent measurements of Nernst,[1] Glaser,[2] Bose,[3] Coehn (*loc. cit.*), and others have shown that, when the measurement is more accurately made, more than one decomposition point may be found under certain circumstances. Such measurements may best be made as follows: The electrode being investigated, together with any other electrode, a galvanometer, and an electromotive force which is changeable at will, are introduced into a circuit. The electrode in question is, furthermore, combined with an auxiliary nonpolarizable electrode. Now in obtaining the current- (or better, current density-) voltage curve, the electromotive forces of the cell,

Auxiliary electrode — Unknown electrode,

are taken as the voltage values. With this arrangement, the nature of the third electrode does not come into consideration because the same electromotive force always corresponds to a definite current density (referred to the unknown electrode) for a given solution. By making the unknown electrode changeable, it is possible by this method to isolate better than formerly the processes which take place at the anode and the cathode, respectively. It has been possible with the use of platinum electrodes to establish two anodic decomposition values, namely,

$$E_A = 1.14 \text{ and } = 1.67 \text{ volts},$$

but only one cathodic value,

$$E_K = 0.0 \text{ volt},$$

for a 1 normal solution of an acid.

The question now arises, how can the existence of this lower value of the decomposition point of water be explained? In addition to the assumption previously made that the decomposition potential of 1.67 volts is the result of supersaturation phenomena, and, as observed, varies with the material of which the electrode is composed, it may be stated that even ordinary platinum electrodes pos-

[1] *Ber.*, **30**, 1547 (1897). [2] *Ztschr. Electrochem.*, **4**, 355 (1898).
[3] *Ztschr. Electrochem.*, **5**, 153 (1898).

sess, although a very slight, yet a sufficient degree of reversibility to produce a continuous decomposition at 1.14 volts which is distinctly detected by very exact measurements. The reversibility may be due to the formation of an intermediary compound between oxygen and water. The decomposition value of 1.14 volts is that of the reversible reaction,

$$4\,OH' + 4\,\underline{\varrho}\,(+) \rightleftarrows 4\,OH \rightleftarrows 2\,H_2O + O_2,$$

when the oxygen is at atmospheric pressure and the hydrogen ion concentration is 1 normal.

The lower anodic decomposition value then corresponds to a reversible process, while the higher value is plainly due to the supersaturation phenomena. This is in agreement with the fact that the former value is independent[1] of, and the latter value dependent upon, the electrode material. The process corresponding to the value 1.67 volts may be represented as follows:—

$$4\,OH' + 4\,\underline{\varrho}\,(+) \rightleftarrows 4\,OH \rightleftarrows H_2O + O_2 \rightarrow \underline{O_2},$$

where O_2 represents traces of oxygen dissolved to a high concentration, and $\underline{O_2}$, oxygen at atmospheric pressure. The part of the process indicated by the single arrow can proceed in but one direction and is accompanied by a loss in free energy.

It might be expected that metals which exhibit a considerable over-voltage in respect to the separation of hydrogen would also give a reversible cathodic decomposition point at

$$E_A = 0.0 \text{ volt}$$

in a solution of 1 normal concentration in respect to hydrogen ions. Up to the present time, however, this has not been found to be the case.

It has been endeavored to explain the existence of the two decomposition values given above in another manner, based partly on the assumption, which is certainly theoretically justifiable, that there are present in the water oxygen as well as hydroxyl ions. In this connection see note on page 254. It seems to me that, in order to explain this electrolytic phenomenon, it is not necessary to involve the oxygen ions which are present, if at all, in a very small concentration. In the case of the electrical phenomenon under consideration, it does not appear advisable to involve in the explanations

[1] In view of the irregularities of the oxygen electrode mentioned on page 296, there cannot be a complete independence of the material of the anode.

such slight concentrations as those of the O ions. Haber[1] has with reason pointed out that there are considerable objections to the assumption of even a moderate velocity of formation of ions in the case of such extremely small ion concentrations. This point of view must always be taken into consideration in reference to electrolysis. If by means of the formation of a complex compound, or otherwise, the concentration of an ion falls below a certain value, the separation of this free ion at the electrode is no longer to be assumed. Finally, the results of the experiments of Hofer and Moest[2] also lead to the assumption of the discharge of OH ions at the anode. They found that, during the electrolysis of such mixtures as that of sodium acetate and sodium sulfate, besides ether and carbon dioxide, methyl alcohol was formed in considerable quantities at the anode. This formation of methyl alcohol can scarcely be explained otherwise than on the assumption of a direct union of OH- and CH_3-radicals.

By the very recent investigations of Grafenburg,[3] Brand,[4] and Luther and Inglis[5] it has been demonstrated that the electromotive force of an ozone-hydrogen cell at atmospheric pressure and room temperature, using a 1 normal acid solution, is equal to 1.66 volts. The cell is, moreover, reversible. Consequently, in the case of the anode potential,

$$E_h = 1.66 \text{ volts},$$

we have a third characteristic point which corresponds to a reversible process and which is also independent of the nature of the material of the noble anode. In the case of platinum this point is nearly identical with the second decomposition point already mentioned. At the present time it is not possible to give a scheme representing the electrolytic formation or decomposition of ozone.

Finally, there is another result obtained in the investigation mentioned on page 305 which is of great interest. It was found that still other anode decomposition values may be detected above the value 1.67 volts. When sulfuric acid, for example, is electrolyzed between platinum electrodes, four such values have been found, namely,

$$E_{h\ \text{electrode-electrolyte}} = 1.14;\ 1.67;\ 1.95;\ \text{and } 2.6 \text{ volts}.$$

At each of these points, the electrolysis receives a sudden acceleration. A similar behavior may also be observed in the case of bases. These results seem to indicate that other ions besides hydrogen and

[1] *Ztschr. Elektrochem.*, **10**, 443 and 773 (1904). [4] *Drud. Ann.*, **9**, 468 (1902).
[2] *Liebigs Ann.*, **323**, 304 (1902). [5] *Ztschr. phys. Chem.*, **43**, 203 (1903).
[3] *Ztschr. Elektrochem.*, **8**, 297 (1902).

hydroxyl ions take part in the electrolysis. It would seem probable that the value 1.95 volts corresponds to that point at which the sulfate ions, and the value 2.6 volts to that at which the acid sulfate ions, begin to take part in the electrolysis. It may further be concluded from these results that the velocity of formation of hydrogen and hydroxyl ions cannot be especially great, for otherwise it would not have been possible to find the above decomposition points. This leads to the conclusion that the hydrogen and oxygen set free by the action of strong electric currents is, to a great extent, of secondary origin, resulting from the action of the liberated radicals on the water.

In the following table the values of the anodic decomposition voltage, $E_{\text{electrode-electrolyte}}$, (except at the point 1.14 volts) for a number of acids are given:—

Acid	C_n	Decomposition Voltages		
		First	Second	Third
Nitric	2.3	1.66	1.88	—
Phosphoric	2.3	1.67	1.96	2.18
Formic	3.5	1.69	1.88	—
Acetic	3.5	1.67	2.05	—
Propionic	3.5	1.68	2.20	—
Butyric	3.5	1.67	2.35	—
Valerianic	3.5	1.67	—	—
Tartaric	1.2	1.66	1.85	2.2
Benzoic	saturated	1.67	2.00	—
Phthalic	saturated	1.68	1.97	2.6

The assumption just made that each decomposition voltage, or, in other words, each factor of irregularity of the current-voltage curve, indicates that a new reaction is beginning to take place is, in a way, confirmed by the investigation of Bose (*loc. cit.*, Figure 51). As an electrolyte, he used a 0.965 normal solution of hydrochloric acid to which various quantities of potassium bromide had been added. When the bromine ion concentration was large, he obtained but one anode decomposition point, namely, that of the bromine ions. Likewise when the bromine ion concentration was small, only a single value was obtained, this time that of the chlorine ions. Only at a definite concentration of the bromine ions (0.001 n. KBr) did he obtain both the value for bromine ions and that for chlorine ions

(see the two breaks in curve IV). Between these two turning points the curve follows first a vertical, then a moderately upward sloping direction, which in many cases becomes completely horizontal and even may slope downward again. It is assumed that the curve follows such a horizontal course when the primary substance which is disappearing during the electrolysis is nearly consumed at the electrodes.[1]

ANODIC CURVES FOR Br AND Cl SEPARATION FROM HCl CONTAINING SOLUTIONS OF KBr

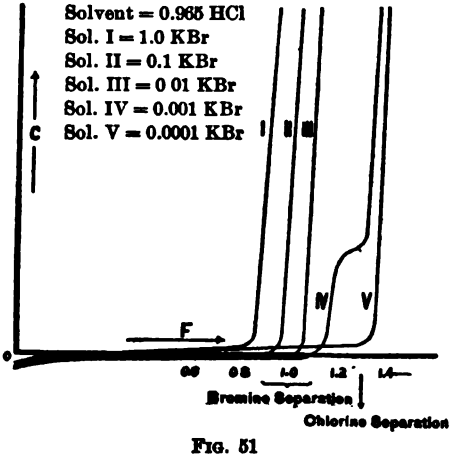


FIG. 51

To be sure, it should be taken into consideration that in these experiments the appearance of a new turning point in the curve is accompanied by the appearance of a new phase at the electrode, while in earlier cases a new phase could not be detected. The significance of the former turning points is, therefore, not yet established with certainty. However, according to Luther and Brislee[2] it is possible that in many cases the different turning points do not correspond to different processes taking place in the electrolyte, but to different changes taking place as time passes on the surface of the electrode. This agrees with the remarks made on page 301 in regard to the potential of the electrodes.

IMPORTANCE OF THE DECOMPOSITION VOLTAGE IN MAKING ELECTROLYTIC SEPARATIONS AND IN PREPARING NEW COMPOUNDS

As already shown, different decomposition points characterize the various metals. From this fact it was inferred by Le Blanc that it should be possible to quantitatively precipitate[3] metals one after another from their mixed solutions by a gradual increase in the

[1] See also the recently published investigation of F. Weigert, *Ztschr. Elektrochem.*, 12, 377 (1906).

[2] *Ztschr. phys. Chem.*, 12, 97 (1893).

[3] *Ztschr. phys. Chem.*, 45, 216 (1903).

electromotive force of the decomposing current. That this may be done has been shown by Freudenberg.[1]

If through a solution containing salts of copper and cadmium a current be passed, the electromotive force of which is insufficient for the continuous deposition of the cadmium but capable of precipitating the copper, the latter metal alone is completely precipitated. When all the copper is precipitated the current ceases, it being thus unnecessary to pay attention to the electrolysis. The electromotive force necessary for the precipitation of the copper increases with the dilution of the solution, according to the formula,

$$\pi = \frac{RT}{v\varrho} \ln \frac{P}{p};$$

but since an increase in dilution from $\frac{1}{10}$ to $\frac{1}{1000000}$ normal (the limit of analytical determinations) causes an increase of less than 0.3 volt for a monovalent and half as much for a divalent metal, this does not hinder the separation if the solution pressures differ moderately from each other.

After the precipitation of the copper the electromotive force may be increased and the cadmium precipitated. In this way a number of separations have become possible, which had not succeeded when attention was given to changing the current-strength instead of the electromotive force. In the future this must be kept in mind in all processes of electrolysis. Complications may, however, arise through the formation of alloys or of chemical compounds, which may prevent a complete separation.

Besides the neutral or acid solutions, those of the double compounds of the metal salt with ammonium oxalate or potassium

[1] It should, however, be noted that about ten years ago M. Kiliani called attention to the possibility of electrolytic separations by a gradation of the electromotive force, and carried out the separation of silver and copper. He came upon the idea in considering the heat effects characterizing individual metals, and calculated from them the electrical energy necessary for their precipitation. This method of calculation has been shown to be inapplicable, for which reason, and perhaps more especially because of the general uncertainty regarding polarization conditions introduced, his work did not receive much attention. That when the electromotive force is above a certain value a metal may be continuously precipitated from its solution, while below this point only an analytically negligible or absolutely unweighable amount precipitates, was not at that time clear. The opinion was then much more commonly held that even with low electromotive forces not inconsiderable quantities of the metal were precipitated, according to which view the separation of two metals by a proper regulation of the electromotive force appeared as an accident rather than as a necessary result of recognized relations.

cyanide are especially adapted to such separations. In the latter many metals can be separated from one another which cannot be separated in acid solution. Thus in acid solution platinum cannot be separated from gold, mercury, and silver, *i.e.* from the metals with slightly different solution pressures, but is easily separated in potassium cyanide solution. This depends upon the formation of the complex salt $2\,K^{\cdot}$, $Pt(CN)_6''$, the negative ions of which are dissociated to an extremely slight extent into $Pt^{\cdot\cdot\cdot\cdot}$ and $6\,CN'$. As a result of the extremely low concentration of the ions, the platinum cannot be precipitated by an electromotive force which is sufficient to precipitate the other metals the ions of which are more numerous. Such artifices are also often utilized in technical work, as, for example, in the electrolytic purification of gold.[1] If a warm dilute solution of hydrochloric acid be used as the electrolyte, the gold and platinum of the anode of impure gold go into solution, but only the gold separates at the cathode. The platinum thus becomes accumulated in the solution in the form of complex ions.

Previously, in the quantitative separation of the metals, only the current-strength was altered. In a mixture of zinc, copper, and silver salts in acid solution the silver must separate first, since that process occurs requiring the least expenditure of work, which is also the case even though the electromotive force be very high, provided that sufficient silver ions are present at the electrode. In making this statement it is assumed that the reaction velocities involved are sufficiently great. The current must be stopped at the proper moment, otherwise the second most easily separated metal will be precipitated. After silver and copper, hydrogen follows. To precipitate zinc simultaneously with the latter from an acid solution, the current-strength must be made so great that the hydrogen ions present are insufficient to convey all the electricity from solution to electrode, and zinc ions must take part in the process. It is evidently more rational to choose to regulate the electromotive force instead of the current-strength, whenever possible, for then it is not necessary to watch over the electrolysis. Until within the last few years most electrolytic separations were carried out empirically, without knowledge of these theoretical principles.

Not only the metals, but also the halogens, can, even though not directly, be separated in stages by changing the electromotive force. For further information in regard to these separations, the work of Specketer[2] and E. Müller[3] may be consulted.

[1] *Ztschr. Elektrochem.*, 4, 402 (1898).
[2] *Ztschr. Electrochem.*, 4, 539 (1898).
[3] *Ber.*, 35, 950 (1902).

Thus far in the discussion of the phenomena of polarization attention has been directed chiefly to insoluble electrodes at which the products of electrolysis, especially hydrogen and oxygen, are separated directly from the solution. Attention will now be given to those cases in which the product of electrolysis reacts either with the electrode itself or with some substance in its vicinity. A general idea of such cases may be obtained from the following consideration: —

Whenever the evolution of hydrogen or oxygen at the electrodes is prevented, *depolarization* is said to have taken place. *Depolarization may then consist of a reduction at the anode or of an oxidation at the cathode.* When the electrodes are thus freed of hydrogen and oxygen, the electromotive force which is required to effect a continuous decomposition is less than that required before they were freed. This may easily be shown by a determination of the electrode potentials. This decrease is due to the fact that the two gases can no longer accumulate to high concentrations at the electrodes, but must react with the substance, or depolarizer, in question while at a low concentration. The more energetic the depolarizer (or mixture of depolarizers), the lower is the concentration of the hydrogen and oxygen at the electrodes, and consequently the lower is the electromotive force required to carry on the electrolysis. Indeed, in many cases a spontaneous electrolytic process results, and the cell, of itself, produces electrical energy.

The velocity with which the hydrogen and oxygen are consumed naturally plays an important part. For example, an oxidizing agent which, for small currents, appears much stronger than another, may for large currents appear much weaker. The following general statement may be made: —

An oxidizing or a reducing agent is electromotively active in proportion to its power of reducing the concentration of the separated hydrogen or oxygen.

The electromotive activity itself is dependent on the concentration of the depolarizer at the electrode, and therefore indirectly on the rapidity of stirring, the velocity of diffusion, and the current density in the case of depolarizers which react rapidly, and on the specific character of the depolarizer, catalytic action, and above all, on the temperature in the case of depolarizers which react slowly. These points have already been touched upon in the discussion of electro-chemical reactions on page 281.

In the above consideration, it has been assumed that hydrogen and oxygen first actually separate and then react with the depolar-

izer. In many cases this may be true, but in others it certainly is not true. For instance, if zinc is made an anode in a dilute solution of sulfuric acid, it is very improbable that the formation of zinc ions is the result of a secondary reaction between zinc and the separated oxygen. It is universally assumed that the zinc ions are formed directly. The above method of viewing the phenomena of depolarization is, however, allowable if it is only desired to obtain a clear idea of the formation of potential-difference at the electrodes, providing, however, that a state of equilibrium exists, *i.e.* that all of the potential-differences existing at the electrode are equal. (See also pages 263 to 267.)

Oxidizing and reducing agents are extensively used in electrolysis on a commercial scale with more or less success in order to decrease the electromotive force required and thus to effect a saving in electrical energy. Naturally in this case it is of first importance that the cost of the substance used as a depolarizer be not greater than the resulting saving in electrical energy. In his well-planned process for the refining of copper, Höpfner makes use of a solution of sodium and ferric chlorides. This solution dissolves the copper from its ores in the cuprous state with the simultaneous reduction of the ferric to ferrous chloride. This copper-containing solution is sent through the cathode compartment of the electrolytic apparatus, where the copper is deposited. It is then sent to the anode compartment, where the ferrous iron is oxidized to the original ferric state. The solution may now be passed through the same cycle again. By the reducing action of the ferrous chloride at the anode the separation of chlorine and the corresponding high electromotive force is avoided.

Soluble electrodes are used to attain the same end, namely, the saving of energy.

The nature of the reacting substances and the conditions of the experiment determine which specific reactions will take place in any individual case. By the electrolysis of alkali chlorides, for instance, it is possible to obtain metal and chlorine, alkali liquor and chlorine, hypochlorite, chlorate, or perchlorate. Although considerable success has already been attained, this is still a field of great promise for experimental research. Space in this book is too limited for a consideration of specific cases, hence the student is referred to the compilation of F. Förster, "Elektrochemie wässerigen Losungen" (1905). Here we must confine ourselves to the more general points of view and their characterization by citation of individual cases.

From one and the same substance, it is possible, especially in organic chemistry, by means of simple oxidation to obtain different new substances which, under comparable circumstances, exhibit different oxidation voltages. If now this original substance be used as a reducing agent at the anode, it is evident that, according to the magnitude of the applied anode potential, the first, second, third, and perhaps still higher oxidation stages of the compound may be formed. In such a case the determination of the decomposition voltages might be of great importance. Each decomposition point indicates the beginning of a new reaction. If it is desired to exclude the product of one of the reactions, the electrolysis must be carried out with an electromotive force which is less than the decomposition voltage which corresponds to this reaction.

In this manner, Coehn[1] was able, by passing a stream of acetylene through the anode compartment during the electrolysis of potassium hydroxide under an electromotive force which was between the first and the second decomposition points, to demonstrate that as a matter of fact formic acid may thus be formed quantitatively. Hence in this case the entire electrical work was expended in the formation of formic acid. If a higher electromotive force be employed, a mixture of substances is obtained, in which carbon dioxide, formic acid, and oxygen have been found.

This method for the preparation of formic acid is of interest in that it indicates how a substance may be prepared without the formation of troublesome by-products. Unfortunately there is but slight probability that this process will become of value commercially, because with the limited electromotive force, the available current density is very small, and therefore the quantity of formic acid formed per unit of time is insignificant compared with the size of the necessary apparatus.

Previous to this work of Coehn, other similar investigations had been carried out, especially by Haber.[2] He succeeded in showing that by reducing nitrobenzene at a given electrode with the use of different constant electromotive forces, different products are obtained.

It is evident that in many cases it is of importance to find some means of increasing the potential at which, for a given current density, oxygen is evolved. With such a means at hand, it might be possible that other oxidations, which are desired, would take place for which the previous potential was either quite too low or at

[1] *Ztschr. Elektrochem.*, **7**, 681 (1901).

[2] *Ztschr. Elektrochem.*, **4**, 506 (1898); *Ztschr. phys. Chem.*, **32**, 193 (1900).

least too low for a good yield of the desired oxide. Such a means has been found in the form of fluorine ions. It is a fact that the yield of oxidation processes taking place at a platinum anode is considerably increased by the presence of these ions.

If, after a knowledge of the facts described above has been obtained, the catalytic influence of the electrode material upon the formation of new substances mentioned on page 275 be recalled to mind, the thought is at once suggested that the different potentials existing at the electrodes during the passage of an electric current is the cause of this different or catalytic behavior of the metals. This subject is elucidated by the recently published work of Haber and Russ.[1] In this work they have shown that velocity of reduction at the surfaces of different metals is very different even for the same voltage. The specific influence of the material of the cathode plainly follows as a consequence of this fact. They investigated especially the depolarizing action of the substances:—

Nitrobenzene, *p*-Nitrophenol,
Hypochlorite, and Quinhydrone,

at electrodes of

Gold, Platinum,
Silver, Iron,
and Nickel.

Furthermore, they were able to confirm the peculiar influence which in many cases the past treatment of an electrode exerts upon the electrolytic process. By subjecting an electrode to continuous cathodic polarization, it may be made "active," *i.e.* the rapidity of depolarization at it may be increased. This increase in activity becomes evident in the following manner: Starting with a definite current and a definite electrode potential, such that hydrogen is rapidly evolved, it may be observed that the current increases, the potential falls, and the evolution of hydrogen slackens or ceases. This active state is very unstable. A short interruption of the current is sufficient to restore the original state of the metal.

Summing up, the conclusion is reached that the catalytic influence of the electrode material, as well as the electromotive force, plays an important part in the electrolytic process. This is shown also by the recent investigation of Tafel and Naumann[2] on the electrolytic reduction of coffeine and succinic imide. The process can be carried out only with the use of a cathode of cadmium, mercury,

[1] *Ztschr. phys. Chem.*, 47, 257 (1904).
[2] *Ztschr. phys. Chem.*, 50, 713 (1905).

or lead. In the case of the latter metal, the cathode potential must not exceed a certain value. This fact shows clearly the influence of potential on the process. The influence of the electrode material is shown by the fact that with the same cathode potential the reducing action obtained with mercury is different from that obtained with lead. The latter influence also occurs in the process mentioned on page 280, involving PbO_2.

The phenomena of the electrolysis of fused salts are, as shown by the investigations of R. Lorenz,[1] entirely analogous to those of aqueous solutions.

Electrolysis with an Alternating Current.[2] — If, instead of a direct current, a symmetrical alternating current be used, it is at once evident that, with so-called reversible electrodes, no change would be detected either in the solution of the electrolyte or at the electrodes. The change which is produced by the momentary flow of electricity in one direction is exactly compensated by that produced by the next momentary flow in the opposite direction. On the other hand, if the electrolysis is carried out with such an arrangement as:

Copper — Acid solution of sodium sulfate — Copper,

whether or not copper goes into the solution depends upon the rapidity of alternation. If the current be but slowly alternated, a greater or less quantity of copper ions sent into the solution by the momentary current in one direction is removed from the immediate vicinity of the electrode by diffusion or convection so that an insufficient quantity of these ions are available at the electrode for precipitation by the next momentary flow of electricity in the opposite direction, then this deficit is supplied by hydrogen or sodium ions. Experiments have shown that for a current density of 0.046 ampere per square centimeter and a frequency of alternation of 1000 per minute and higher, only a small per cent of copper goes into solution. The same holds for the system,

Platinum — Sulfuric acid — Platinum.

[1] See also Le Blanc and Brode, "The Electrolysis of Fused Sodium and Potassium Hydroxides," *Ztschr. Elektrochem.*, **8**, 697 (1902). More detailed information will be found in Lorenz's "Die Elektrolyse geschmolzener Salze," Volumes **20**, **21**, and **22** of the "Monographien über angewandte Elektrochemie," W. Knapp, publisher, Halle, Saxony.

[2] Le Blanc and Schick. *Ztschr. phys. Chem.*, **46**, 213 (1903); A. Löb, *Ztschr. Elektrochem.*, **12**, 79 (1906). The reader is referred also to the interesting experiments of Drechsel, *J. prakt. Chem.*, **29**, 34, and 38, which cannot be considered here.

In this case the quantity of hydrogen and oxygen evolved by an alternating current of high frequency is practically equal to zero.

The relations are quite different when, for instance, two copper electrodes are placed in a 4 normal solution of potassium cyanide. In this case, with an alternating current of a frequency of 1000 per minute, the copper dissolves in the form of cuprous ions almost quantitatively, accompanied by the evolution of an equivalent quantity of hydrogen. Thus the same results are attained as with the direct current. As the frequency of the alternating current is increased, the quantity of copper dissolved decreases. However, when the frequency has reached 38,000 reversals per minute, and the current density is 0.046 ampere per square centimeter, the yield is still about 33 per cent.

The most probable explanation of this phenomenon is found in the formation of complex substances. Copper ions may unite with potassium cyanide, or cyanide ions, to form a complex ion from which copper cannot be separated at the cathode. If now the reversal of the current is so slow that the copper ions sent into the solution by the momentary current in one direction have sufficient time to form the complex ion with the cyanide ion, the reverse current cannot redeposit the copper. The greater the frequency of reversal of the current, the greater is the per cent of copper sent into the solution which will be deposited out again. This offers a means of obtaining an idea of the velocity of a reaction between ions. Thus the reaction between copper ions and potassium cyanide during the electrolysis of a 4 normal solution of potassium cyanide between copper electrodes, with a current density of 0.046, is practically completed in $\frac{1}{1000}$ of a minute, while at the end of $\frac{1}{5000}$ of a minute it has not proceeded far enough to be detected. The alternating current also throws some light on the velocity of the formation of difficultly soluble precipitates, although in most cases the precipitate formed by the current in one direction is completely decomposed again by that in the opposite direction.

It will only be mentioned here that with the alternating current remarkable passivity phenomena occur.

Electrolysis without Electrodes. — If a platinum cathode be placed in a potassium iodide solution and a platinum anode a few millimeters above the solution, and an electric current from a powerful electric machine be sent from one electrode to the other, then iodine separates at the boundary surface of air and liquid. The quantity of iodine which so separates is that required by Faraday's law.[1]

[1] Klupfel, *Drud. Ann.*, **16**, 574 (1905); Gubkin, *Wied. Ann.*, **32**, 114 (1887).

Hence under these circumstances the negatively charged iodine ions give up their charges to the space occupied by gas or vapor. It is possible that these charges pass through this space to the anode as free electrons. If instead of the anode the cathode be placed above the solution, the corresponding quantity of potassium hydroxide is formed at the surface of the liquid, accompanied by the evolution of hydrogen gas. If, with this same arrangement of electrodes, a solution of a salt of a heavy metal be used, then a separation of metal takes place at the surface. In this case it may be considered that the cathode throws off free negative electrons, constituting cathode rays. The question then at once arises as to the possibility that real cathode rays may have a reducing action on the surface of electrolytes. As a matter of fact, Bose[1] found that, under favorable circumstances, hydrogen is evolved when the surface of a hot saturated alkali solution under a vacuum is exposed to the action of cathode rays. The quantity of hydrogen evolved is, however, considerably greater than required by Faraday's law. Besides the pure electro-chemical action another takes place in this case which may be ascribed to the kinetic energy of the particles of the cathode rays. It may be shown by calculation that the mechanical energy of the cathode rays may, in the most favorable case, produce a much greater chemical action than corresponds to the quantity of electricity involved. Now even if by far the greater part of this energy becomes transformed into heat, the assumption that at least a small portion of this energy is consumed in the evolution of detonating gas is still plausible. The oxygen gas, which would be expected under this assumption, is at first dissolved by the electrolyte. It may, however, with continued action finally be detected.[2]

In the case of the Becquerel rays it is probable that, due to the higher kinetic energy, the dynamical exceeds the purely electro-chemical effect to a greater extent than in the case of the cathode rays.

Decomposition Voltage and Solubility.—That the voltage at which the ions of a salt in a 1 normal solution are separated from the solution marks the upper limit of the solubility of the salt has been pointed out by Nernst.[3] For example, since the decomposition value for iodine ions is

$$E_{\text{c electrode}\leftarrow\text{electrolyte}} = +0.24 \text{ volt},$$

and that of silver ions is

[1] *Ztschr. Wiss. Phot.*, **2**, 223 (1904).

[2] It is also assumed in the case of the formation of ozone that the action of the cathode rays is a purely chemical one. See page 24.

[3] *Ber.*, **30**, 1547 (1897).

$$\underline{E}_{c \text{ electrode} \leftarrow \text{electrolyte}} = +0.49 \text{ volt},$$

silver iodine could not exist in solution to a concentration of 1 normal, because at such a concentration it would become spontaneously decomposed with a force of 0.25 of a volt. Hence in order that silver iodide should be capable of existence, its solubility must be exceedingly small. This is in agreement with facts. If the solubility be calculated for which the decomposition voltage is equal to zero, *i.e.* at which the salt just becomes stable, a value is obtained which is much larger than that actually observed. Bodländer[1] states, what had already been indicated by Luther, that it is possible to calculate exact solubility values if the decomposition voltage of the solid salt be taken into consideration.

Equilibrium constantly exists between the saturated (but dilute) solution of a practically completely dissociated electrolyte and the anhydrous solid salt. Then the work which must be done during electrolysis in order to discharge the ions is equal to that which is required to break up the solid salts into the same constituents at the same concentration. Hence we may consider the decomposition voltage as a measure of the tenacity with which these constituents are held together in the solid state.

The decomposition voltage of the saturated solution is now, at 17°,

$$E_s = 0.0575 \log \left(\frac{P_c}{P}\right)^{\frac{1}{V_c}} + 0.0575 \log \left(\frac{P_a}{P}\right)^{\frac{1}{V_a}}, \tag{1}$$

where P_c and V_c refer to the cation, P_a and V_a to the anion, and P represents the equal concentrations, expressed in equivalents, of the two ions in the saturated salt solution.

The individual decomposition voltages of the cation $\underline{E}_c$ and of the anion $\underline{E}_a$ for an ion concentration of 1 normal is as follows:—

$$\left.\begin{aligned} \underline{E}_c &= 0.0575 \log P_c^{\frac{1}{V_c}}; \\ \underline{E}_a &= 0.0575 \log P_a^{\frac{1}{V_a}}. \end{aligned}\right\} \tag{2}$$

From (1) and (2) the following is obtained:—

$$E_s = \underline{E}_c + \underline{E}_a - 0.0575 \log P^{\frac{1}{V_a} + \frac{1}{V_c}}. \tag{3}$$

If the cation and anion are both univalent,

$$V_c = V_a = 1.$$

[1] *Ztschr. phys. Chem.*, **27**, 55 (1898).

By substituting this value in (3), the following equation is obtained: —

$$\mathfrak{F}_s = \underline{\mathfrak{F}}_c + \underline{\mathfrak{F}}_a - 0.115 \log P.$$

In the case of highly dissociated and slightly soluble electrolytes, the value of P represents the solubility. From this quantity, the values of $\underline{\mathfrak{F}}_c$ and $\underline{\mathfrak{F}}_a$ being known, the free energy $\mathfrak{F}_s Q$ which is liberated during the formation of the solid substance from the corresponding constituents may be calculated. Conversely, the quantities, $\mathfrak{F}_s$, $\underline{\mathfrak{F}}_c$, and $\underline{\mathfrak{F}}_a$ being known, the value of P may be calculated. Of these quantities, $\underline{\mathfrak{F}}_c$ and $\underline{\mathfrak{F}}_a$ are easily determined experimentally, and $\mathfrak{F}_s$ may in many cases be taken as approximately equal to the equivalent heat of formation Q, expressed in calories. Hence

$$\mathfrak{F}_s Q = Q \times 4.189,$$

or

$$\mathfrak{F}_s = \frac{Q \times 4.189}{96540} = \frac{Q}{23045}.$$

Considering the sources of error involved, the calculated values are in remarkable agreement with those actually observed.

Finally, attention is called to an empirical rule which holds in many cases, and which, further, may be established theoretically by deductions from the above equation. It may be stated as follows: —

The solubility of different salts of the same metal (or of the same acid) is the greater, the greater the tendency of the acid radical (or metal radical) to pass from the electrically neutral to the ionized state.

Thus in the case of compounds of the metals, the solubility increases in the order, —

Iodine,
Bromine,
Chlorine,

and in the case of the organic acids, in the order, —

Silver salt,
Acid,
Alkali salt.

Recently, it has been endeavored to bring a large number of properties into relationship with the decomposition voltages.[1]

[1] Abegg and Bodländer, *Ztschr. anorg. Chem.*, **20**, 453 (1899).

CHAPTER IX

SUPPLEMENT

STORAGE CELLS OR ACCUMULATORS

SINCE storage cells are to-day used to an extraordinary extent for many purposes, a brief presentation of the chemical processes which take place in them is here given.

Storage cells or accumulators are arrangements in which electrical energy may be stored as chemical energy, whence it may again be obtained at will in the form of electrical energy. Any reversible cell may be used as an accumulator. If a current be sent through a used Daniell element in the direction from copper to zinc, copper is dissolved and zinc precipitated — in other words, electrical energy is stored up in the form of chemical energy. In practice lead storage cells are used almost exclusively.[1] The electrodes consist of lead plates coated with a specially prepared layer of lead oxide or sulfate, and the electrolyte is 20 per cent sulfuric acid. When a current is sent through this arrangement, lead peroxide (or a corresponding hydrate) is formed on that electrode at which the positive electricity enters the acid, while at the other electrode metallic lead in spongy form is produced. The storage cell is charged after the conduction of sufficient electricity through it. In the discharge both the peroxide and the metallic lead return to sulfate. The chemical process on charging is then essentially the change of lead sulfate to lead at one electrode and to peroxide at the other, while the discharge is simply the return of these substances to lead sulfate. The corresponding heat of reaction is given by Streintz[2] as follows: —

$$PbO_2 + 2H_2SO_4 \text{ aq.} + Pb = 2PbSO_4 + 2H_2O + \text{aq.} + 87{,}000 \text{ cal.}$$

If the electromotive force of the storage cell be calculated from

[1] For particulars concerning the making and use of accumulators, attention is called to the following works: —

Heim, "Die Akkumulatoren" (Oskar Leiner, Leipzig).

Elbs, "Die Akkumulatoren" (Johann Ambrosius Barth, Leipzig).

[2] *Wiener Monatshefte f. Chemie*, 15, 285 (1894).

the known heat of reaction, assuming complete transformation into electrical energy, 1.885 volt is obtained. This agrees very well with the experimentally determined value for dilute sulfuric acid. From this agreement it also follows that the electromotive force of the storage cell is nearly independent of the temperature (page 173), and this has also been demonstrated by Streintz. If this shows that it is probable, the work of Dolezalek[1] removes all doubt, that the process takes place in the manner indicated. Dolezalek showed that the entire behavior of the storage cell is in agreement with the reaction equation. He investigated especially the relation between the electromotive force and the concentration of the acid, and established the fact that the values calculated from thermodynamical considerations agree finely with the values found by experiment, and that therefore (for small current densities) the storage cell is reversible. These results are in complete agreement with the theory advanced by Le Blanc[2] by which the processes taking place in the storage cell were, for the first time, explained with the aid of the ionic theory.

When the storage cell is charged and ready for use, the positive electrode is coated with lead peroxide and the negative with spongy lead. Between the two electrodes is sulfuric acid. It may be assumed that lead peroxide in contact with water forms tetravalent lead ions together with the corresponding hydroxyl ions, and that while the cell is in action the tetravalent ions are transformed into divalent lead ions. *This process is the chief source of the electromotive force of the storage cell.* The tetravalent ions which disappear are constantly replaced from the solid lead peroxide, and the bivalent ions which are formed do not remain in the solution, but since lead sulfate is difficultly soluble, *i.e.* since the product of the concentrations of the divalent lead ions and the sulfate ions is a small value, they combine with the sulfate ions in the solution, forming solid lead sulfate.

At the negative pole metallic lead changes into bivalent ions, a process taking place without producing any considerable potential difference. Here also insoluble lead sulfate is formed from the $Pb^{\cdot\cdot}$ and SO_4''.

The ionic theory not only renders clear the changes of peroxide and metallic lead into sulfate, but also explains the gradual diminution of the electromotive force of the cell in action. While

[1] *Wied. Ann.*, 65, 894 (1898), and "Theorie des Bleiakkumulators," W. Knapp, Halle, Saxony (1901).

[2] First edition of this book, page 223 (1895).

the magnitude of the potential-difference at the positive electrode depends upon the concentration of the quadrivalent and bivalent lead ions (see page 250), that of the potential-difference at the negative electrode depends upon the concentration of divalent lead ions in contact with an excess of metallic lead. The concentration of the quadrivalent ions decreases with time, and that of the bivalent increases, as may be seen from the following: At the peroxide electrode there is a saturated solution of this compound — that is, the product of the concentration of $Pb^{::}$ and the fourth power[1] of the concentration of the OH' ions is here constant. On the other hand, there must be definite relations between these ions and those of the sulfuric acid. The product of the concentration of the H and OH ions in the solution must have a constant value equal to that for water. It has been seen, in the first place, that during the discharge of the cell, lead sulfate is formed at the peroxide electrode, and in the second, that newly formed OH ions produced by the peroxide cannot exist as such, but must combine with the H ions of the acid to form undissociated water. There is thus a continual removal of H and SO_4 ions taking place. The removal of the former allows of an increase in the concentration of the OH ions, and therefore causes a reduction in that of the quadrivalent lead ions. The removal of SO_4 ions permits an increase in the concentration of the $Pb^{\cdot\cdot}$ ions, since the solution is saturated with lead sulfate. This latter process also takes place at the negative electrode. When the supply of peroxide is exhausted, the electromotive force falls very rapidly to an exceedingly low value.

After the cell has been discharged, there is lead sulfate on both electrodes, consequently bivalent lead ions are present. The process of charging consists simply in the change of bivalent lead ions to quadrivalent at the electrode at which the positive electricity enters the solution, and to metallic lead at the other electrode. The $Pb^{\cdot\cdot}$ ions used are replaced from the solid lead sulfate. The $Pb^{::}$ ions and the OH' ions present, having reached that concentration in the solution determined by the dissociation constant for peroxide of lead, combine to form this oxide (or a hydrate). Thus the lead sulfate at one electrode gradually changes into peroxide, and into metallic lead at the other. The opposing electromotive force of the cell increases during the charging, because the processes described as taking place during discharge are reversed. The concentration of the bivalent lead ions at both electrodes diminishes with time, while that of the SO_4'' ions is continually increasing. The concentration of

[1] Because four OH ions correspond to one of the lead ions.

the $Pb^{::}$ ions increases with the increase of H ions formed with equivalent quantities of OH ions from the undissociated water. The OH' ions continually combine with the $Pb^{::}$ to form peroxide, and their concentration must diminish as that of the hydrogen ions increases. The lower the concentration of the OH ions the greater is that of the $Pb^{::}$ ions. If no more bivalent lead ions are present, hydrogen ions separate at one electrode and hydroxyl ions at the other. Thus the rapid generation of hydrogen and oxygen at the electrodes in charging shows that the accumulator is over-charged. In order to cause a considerable generation of hydrogen and oxygen in the cell a somewhat higher electromotive force is required than is necessary to charge it, since the separating gases can accumulate to high concentrations in the electrodes, or, in other words, since the electrodes possess a considerable over-voltage. When platinum electrodes are used in sulfuric acid, an electromotive force of two volts is sufficient to produce a rapid evolution of gas. If this was also the case in the lead cell, the latter could be charged only with a great loss of energy.

The above theory of the processes which take place in the storage cell has received considerable support from the recent work of Elbs and Rixon,[1] which has established the fact that acid which has been in use in such cells contains comparatively large quantities (as much as 0.17 of a gram of $Pb(SO_4)_2$ per liter) of tetravalent lead, and hence of tetravalent lead ions. By a special experiment it was proven that the equilibrium corresponding to the reaction equation, —

$$Pb(SO_4)_2 + 2H_2O \rightleftarrows PbO_2 + 2\ H_2SO_4,$$

is attained in about five hours, when a mixture of freshly precipitated lead peroxide and sulfuric acid is continuously stirred. The presence of the above-mentioned considerable quantity of tetravalent lead in the acid furnishes a plausible explanation of the spontaneous discharge of accumulators. The tetravalent lead migrates from the peroxide electrode, where it is formed, to the spongy lead electrode, where it is reduced to the bivalent state.

It must not, however, be supposed that only the assumed process, especially the formation of tetra- or bivalent lead ions at the anode, takes place. According to Liebenow, it is possible that the ion PbO_2'' is present, and is transformed reversibly into ordinary PbO_2. In describing states of equilibrium, as, for example, in measurements of potential, it makes no difference to which of the reactions of the

[1] *Zeschr. Elektrochem.*, 9, 267 (1903).

equilibrium the source of the electromotive force is ascribed. In describing the process of electrolysis, however, it is absolutely necessary to emphasize the reaction in which the greatest quantities are involved. Which of the reactions this is depends upon the respective velocities of reaction, and must be determined for individual cases. In the case in question it appears more in accord with facts to give prominence to $Pb^{::}$, and not to PbO_2'' ions, because the concentration of the latter is insignificant in comparison with that of the former. (See also page 307.)

Of the storage cells using metals other than lead, the Junger-Edison accumulator is the most interesting.[1] When charged it consists of the combination,

$$Fe - KOH - Ni_2O_3, \text{ aq.}$$

During the charging and the discharging of the cell, the following processes take place: —

$$Fe + 2\ Ni(OH) \rightleftarrows Fe(OH) + 2\ Ni(OH)_2, \text{ or}$$

$$Fe + Ni_2O_3, n\ H_2O \pm r\ H_2O \rightleftarrows FeO, m\ H_2O + (NiO)_2, p\ H_2O.$$

Hence in this cell water plays the greatest part in the reaction. For this reason, but little alkali is required in the cell. This is in contrast to the lead accumulator, in which much sulfuric acid is used.

The normal initial voltage is 1.36 volts. The value of this storage cell in practical service remains to be determined.

ENERGY-EQUIVALENTS (see page 18)

Ergs	Joules	Calories[2]	Kilogram-meters	Liter-atmospheres	Kilowatt-hours	Horse-power
1	10^{-7}	2.387×10^{-8}	1.020×10^{-8}	9.872×10^{-10}	2.778×10^{-14}	3.776×10^{-14}
10^7	1	0.2387	0.1020	9.872×10^{-3}	2.778×10^{-7}	3.776×10^{-7}
4.189×10^7	4.189	1	0.4272	4.135×10^{-2}	1.164×10^{-6}	1.582×10^{-6}
9.806×10^7	9.806	2.341	1	9.861×10^{-2}	2.724×10^{-6}	3.703×10^{-6}
1.013×10^9	101.3	24.18	10.33	1	2.814×10^{-5}	3.825×10^{-5}
3.600×10^{13}	3.600×10^6	8.593×10^5	3.672×10^5	3.553×10^4	1	1.359
2.649×10^{13}	2.649×10^6	6.325×10^5	2.702×10^5	2.616×10^4	0.7360	1

[1] Elbs, *Ztschr. Elektrochem.*, 11, 734 (1905); Gräfenberg, *Ztschr. Elektrochem.*, 11, 736 (1905); Zedner, *Ztschr. Elektrochem.*, 11, 809 (1905); Förster, *Ztschr. Elektrochem.*, 11, 948 (1905). See also the discussion following the above papers.

[2] The calorie (15° gm-cal.) here is that recommended by the International Congress for Applied Chemistry at Berlin, namely, equal to 4.189×10^7 ergs.

ELECTRO-CHEMICAL CONSTANTS (see page 43)

M_{ec} represents electro-chemical equivalents, or the quantity or mass of substance in milligrams which is separated by one ampere-second, and $3600 \cdot M_{ec}$ represents the quantity or mass in grams of various anions and cations which is separated by one ampere-hour of electricity (= 0.0373 equiv.).

Cations	Equiv.	M_{ec}	$3600 \cdot M_{ec}$	Anions	Equiv.	M_{ec}	$3600 \cdot M_{ec}$
$\frac{1}{3}$ Al	9.03	0.09354	0.3367	Br	79.96	0.8282	2.982
$\frac{1}{5}$ Sb	40.07	0.4151	1.494	BrO_3	127.96	1.325	4.772
$\frac{1}{5}$ As	25.	0.2590	0.9322	Cl	35.45	0.3672	1.322
$\frac{1}{2}$ Ba	68.7	0.7116	2.562	ClO_3	83.45	0.8644	3.112
$\frac{1}{2}$ Pb	103.45	1.072	3.858	CHO_2	45.01	0.4662	1.678
$\frac{1}{2}$ Cd	56.2	0.5821	2.096	$C_2H_3O_2$	59.02	0.6114	2.201
$\frac{1}{2}$ Ca	20.05	0.2077	0.7477	CN	26.04	0.2697	0.9710
$\frac{1}{3}$ Cr	17.37	0.1799	0.6477	$\frac{1}{2}$ CO_3	30.00	0.3106	1.119
$\frac{1}{2}$ Fe	27.95	0.2895	1.042	$\frac{1}{2}$ C_2O_4	44.00	0.4558	1.641
$\frac{1}{3}$ Fe	18.63	0.1930	0.6947	$\frac{1}{2}$ CrO_4	58.05	0.6013	2.165
$\frac{1}{3}$ Au	65.73	0.6806	2.451	Fl	19.	0.1968	0.7085
K	39.15	0.4055	1.460	I	126.97	1.315	4.735
$\frac{1}{2}$ Co	29.5	0.3056	1.100	IO_3	174.85	1.811	6.520
Cu	63.6	0.6588	2.372	NO_3	62.04	0.6426	2.313
$\frac{1}{2}$ Cu	31.8	0.3294	1.186	$\frac{1}{2}$ O	8.	0.08287	0.2983
Li	7.03	0.07282	0.2621	OH	17.01	0.1762	0.6343
$\frac{1}{2}$ Mg	12.18	0.1262	0.4542	$\frac{1}{2}$ SiO_3	38.20	0.3957	1.424
$\frac{1}{2}$ Mn	27.5	0.2849	1.025	$\frac{1}{2}$ S	16.03	0.1660	0.5978
Na	23.05	0.2388	0.8595	$\frac{1}{2}$ Se	39.6	0.4102	1.477
$\frac{1}{2}$ Ni	29.35	0.3040	1.094	$\frac{1}{2}$ SO_4	48.03	0.4975	1.791
Hg	200.0	2.072	7.458	$\frac{1}{2}$ Te	63.8	0.6609	2.379
Ag	107.93	1.118	4.025				
$\frac{1}{2}$ Sr	43.8	0.4537	1.633				
$\frac{1}{2}$ Te	31.9	0.3304	1.190				
Tl	204.1	0.2114	0.7611				
H	1.006	0.01044	0.03759				
$\frac{1}{2}$ Zn	32.7	0.3387	1.219				
$\frac{1}{2}$ Sn	59.5	0.6163	2.219				
$\frac{1}{2}$ Sn	29.75	0.3082	1.109				

APPENDIX

NOTATION

SINCE there is no recognized system of notation in electrochemistry, it has been endeavored in this translation to devise and introduce a system of notation which shall be simple, and shall avoid the difficulty and confusion often caused by the use of complicated or unsystematized notation. While the system given here is original as a whole, yet in nearly every case the individual symbols have been used with a similar meaning in some other work on chemical or electrical science. Hence it will scarcely be necessary for any one at all familiar with chemical or electrical literature to study the system. It is also believed that students and general readers of the book will experience no difficulty or confusion in keeping the notation in mind.

In devising the system, each class of properties, quantities, etc., has been represented by a Roman letter which, while avoiding ambiguity, readily suggests the class in question. Thus concentration has been represented by the letter *C*, and dilution by the letter *D*. Whenever the names of two or more classes have the same initial letter, the use of a single character to represent them has been avoided by the use of small letters, small capitals, and large capitals, or of different letters which may be substituted for the initial letters without materially affecting the sound of the class names. This may be illustrated by the following examples:—

Concentration (of a gas)	$= c$
Current (electric)	$= \mathrm{c}$
Concentration (of a solid or liquid)	$= C$
Conductance (electrical)	$= \mathrm{K}$
Constant	$= K$

The class notation adopted is given in the following table:—

A . . . ACIDITY.

B . . . BASICITY.

c . . . ELECTRIC CURRENT. $\left(= \frac{\mathrm{E}}{\mathrm{R}}.\right)$

C . . . Concentration. $\left(=\frac{1}{D}.\right)$

d . . . Differental.

D . . . Diffusion.

D . . . Dilution. $\left(=\frac{1}{C}.\right)$

E . . . Energy.

F . . . Force. (Factor or function $= f$.)

H . . . Heat or Heat Capacity.

K . . . Electrical Conductance. $\left(=\frac{1}{R}.\right)$

K . . . Constant. (Capacity $= k$).

l . . . Length, Height, Distance.

M . . . Mass or Weight.

n . . . Number. (Normal concentration $= N$.)

P . . . Pressure.

Q . . . Quantity.

R . . . Electrical Resistance. $\left(=\frac{E}{C}.\right)$

R . . . Gas and Solute Constant. $\left(=\frac{pv}{nT}.\right)$

s . . . Surface or Cross Section.

S . . . Solubility.

T . . . Time.

T . . . Temperature.

U . . . Velocity.

V . . . Valence or Number of Charges on an Ion.

V . . . Volume.

W . . . Work.

x . . . Fractional Part. Degree of Dissociation.

It should be noted that electrical quantities are in general represented by small capitals.

The whole system is based on the class notation just given, the individual members of a class being represented by the class letter with distinguishing sub letters. This is illustrated by the following example:—

Concentration (general)	$= C$.
Concentration in grams per liter	$= C_g$.
Concentration in equivalents per liter	$= C_e$ or C_n.
Concentration in mols per liter	$= C_m$.

In the case of conductance, a different rule has been followed. The various kinds of conductances have been distinguished as follows:—

Conductance (general) = K.
Specific Conductance = $\underline{K}$.
Equivalent Conductance = $\underline{\underline{K}}$.

Symbols have been distinguished by an underline also in the following cases:—

Quantity of Electricity (general) = Q.
Quantity of Electricity, 96540 coulombs = $\underline{Q}$.
Quantity of Heat (general) = Q.
Quantity of Heat, 1 calorie = $\underline{Q}$.
Electromotive Force (general) = E.
Single Potential-difference = $\underline{E}$.

The complete system of notation is given in alphabetical order in the following table:—

a . . . Acceleration.

A . . . Acidity.

B . . . Basicity.

c . . . Concentration of a gas. $\left(=\frac{1}{d}.\right)$

- c_g Grams per liter.
- c_m Mols per liter.
- c_e Equivalents per liter.

c . . . Electric current or current-strength. $\left(=\frac{E}{R}.\right)$

C . . . Concentration of a solute. $\left(=\frac{1}{D}.\right)$

- C_g Grams per liter.
- C_e Equivalents per liter.
- C_m Mols per liter.

d . . . Differential.

d . . . Dilution of a gas. $\left(=\frac{1}{c}.\right)$

D . . . Dilution of a solute. $\left(=\frac{1}{C}.\right)$

- D_g Volume in liters containing one gram.
- D_e Volume in liters containing one equivalent.
- D_m Volume in liters containing one mol.

D . . . Diffusion.
  D_{ee} Coefficient.

E . . . Energy.
  E_e or E Electrical energy.
  E_{ex} External energy.
  E_f Free energy.
  E_h Heat energy.
  E_{in} Internal energy.
  E_m Mechanical energy.
  E_v Volume energy.

f . . . Factor (or function).

F . . . Force.
  F_e or F Electromotive force.
    F_c Referred to the standard calomel cell.
    F_h Referred to the standard hydrogen cell.
    F Single potential-difference.
    F_c Single potential referred to calomel cell.
    F_h Single potential referred to hydrogen cell.
    F_0 or (EP) Single potential at unit concentration.
  F_m Mechanical force (pressure).

H . . . Heat or heat capacity.
  H_e Electrical heat effect (Joule's heat effect).
  H_r Heat of reaction.
  H_d Heat of dissociation.
  H_n Heat of neutralization.

k . . . Electrical capacity.

K . . . Electrical conductance.
  K Specific conductance or conductivity.
  K Equivalent conductance.

K . . . Constant.
  K_c Cell constant.
  K_d Dissociation constant.
  K_e Equilibrium constant.
  K_D Dielectric constant.
  K_s Solubility constant.
  K_v Velocity constant.

l . . . Length, height, or distance.

m . . . Mass or weight of a gas.
  m_{at} Atomic mass in grams (gram-atom or atom).
  m_m Molecular mass in grams (gram-mol or mol).

M . . . Mass or weight of a solute, liquid or solid.
- M_{at} Atomic mass in grams (gram-atom or atom).
- M_{eq} Equivalent mass in grams (gram-equivalent or equivalent).
- M_i Ion mass in grams (gram-ion or ion).
- M_m Molecular mass in grams (gram-mol or mol).

n . . . Number.
- n_a Transference number for anions ($=1-n_c$).
- n_c Transference number for cations ($=1-n_a$).
- n_i Number of ions formed from one molecule of an electrolyte.
- n_m Number of molecules formed from one molecule.

N . . . Normal concentration.

p . . . Pressure of a gas.

P . . . Electrolytic solution pressure.

P . . . Pressure of a solute, *i.e.* solute or osmotic pressure.

q . . . Quantity of magnetism.

Q . . . Quantity of electricity.
- $\underline{\mathrm{Q}}$ Electro-chemical unit of quantity of electricity, *i.e.* 96540 coulombs.

Q . . . Quantity of heat.
- $\underline{Q}$ Quantity of heat required to raise the temperature of one gram of water one degree, *i.e.* 1 calorie.

r . . . Internal electrical resistance of cells.

R . . . Electrical resistance. External resistance of a circuit

R . . . Gas or solute constant. $\left(=\frac{pv}{nT}.\right)$

s . . . Surface or cross section.

S . . . Solubility.

t . . . Temperature, centigrade scale.

T . . . Time.
- T_d Time in days.
- T_h Time in hours.
- T_m Time in minutes.
- T_s Time in seconds.

T . . . Temperature, absolute scale.

U . . . Migration velocity of ions.
- U_a Of anions.
- U_c Of cations.

U_s . . . Velocity of solution.

U_r . . . Velocity of reaction.

v . . . Volume of a gas.

v . . . Valence. Number of electrical charges on an ion.

V . . . Volume of a liquid or solid.

W . . . Work.

- W_m Mechanical.
- W_e Electrical.
- W_π Osmotic.

x . . . Fractional part. Degree of dissociation.

Δ . . Fractional change.

- Δ_t Due to temperature change of one degree.

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